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**REPORT NO. 45**

**HYDROGEN PEROXIDE**

**PART FOUR**

**CHAPTER 9 - STABILIZATION**

**CHAPTER 10 - ANALYTICAL PROCEDURES**

**CHAPTER 11 - USES**

**CHAPTER 12 - INORGANIC PEROXY COMPOUNDS**

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**A Monograph Prepared with  
Support from the  
Office of Naval Research  
Contract No. N5ori-07819  
NR-092-008**

**BY**

**W. C. Schumb  
C. N. Satterfield  
R. L. Wentworth**

**MASSACHUSETTS INSTITUTE OF TECHNOLOGY  
Departments of Chemistry and Chemical Engineering Cambridge, Mass**

**Division of Industrial Cooperation Project 6552  
November 1, 1953**

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## PREFACE

A program of fundamental studies of the properties, formation and reactions of hydrogen peroxide has been sponsored at M. I. T. since 1945 by the U. S. Navy, Bureau of Ordnance, and later the Office of Naval Research. For some time it has been apparent that the growth of basic knowledge of this chemical, as well as the development of various practical applications, would be furthered by a compilation and evaluation in the form of a monograph of the scientific and technical knowledge available.

The present report constitutes Part IV (Chapters 9 - 12) of such a monograph. The remaining parts (I, II and III) bear the Report Numbers 42, 43 and 44. Report No. 42 was issued September 15, 1953, and Reports 43 and 44 will be issued in the near future. The Table of Contents presented in this report gives a detailed outline of the material presented in Part IV and indicates the contents of the other three parts by listing the headings of the chapters which each of them will contain.

Literature appearing up to August 1, 1953 has been consulted in the preparation of Part IV of the monograph. It has not been attempted to cite every reference on hydrogen peroxide, but all publications which appeared to the authors to have some present-day usefulness are quoted. Patents have been treated in the same fashion as other publications and it has not been attempted to prepare an exhaustive list of them.

Arrangements have been made for this monograph subsequently to be published in book form. The authors will appreciate errors being called to their attention or receiving the comments of readers on the material presented.

Walter C. Schumb  
Charles N. Satterfield  
Ralph L. Wentworth

November 1, 1953

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## CHAPTER NINE

### STABILIZATION

It has been well established by the work of various investigators that pure hydrogen peroxide, or aqueous solutions thereof, in the absence of contaminating catalysts and in a thoroughly clean container of non-catalytic material, is a very stable material, even at temperatures of 50°C. or somewhat higher. At 100°C., decomposition to the extent of about 2% in 24 hours has been observed for 90 wt. % hydrogen peroxide (1). At room temperature, 90% unstabilized aqueous solutions have been kept for many months with less than 1% decrease in the hydrogen peroxide contents. However, the rate of decomposition increases exponentially with temperature and at the boiling point--approximately 140°C. for 90% hydrogen peroxide--rapid decomposition ensues and the heat released causes the concentrated solution to boil. Although as stated, the rate of decomposition of perfectly pure hydrogen peroxide in very concentrated solutions (90 - 98%) is known to be very low, the attainment of such ideal conditions as perfect purity and the absence of all catalytic effects from the walls of the containing vessel or from dissolved or suspended impurities, is, of course, practically impossible, and the best available data on the intrinsic stability of hydrogen peroxide must be considered only as approximations to those ideally attainable.

Representative data, obtained with high quality unstabilized hydrogen peroxide, indicate a decomposition rate at 50°C. of 90% hydrogen peroxide not in excess of 0.0010 percent per hour and possibly significantly lower than this. In the presence of a small quantity of a stabilizer, such as sodium stannate, or 8-hydroxyquinoline pyrophosphate, this figure may fall to the order of magnitude of 0.0003 percent per hour at 50°C.

The corresponding value at 30°C. would be approximately 0.00006 percent/hour, or about 0.5% per year. Careful measurements on unstabilized hydrogen peroxide at lower concentrations, obtained by dilution of the purest available concentrated solutions with very pure water, indicate that the percentage decomposition rate increases but slightly over the range 95 to 40% hydrogen peroxide. However, unless the dilution water is rigorously purified and great care exercised in the dilution procedure to avoid access of contaminants, the decomposition rate of the diluted material may show a marked increase over that of the most concentrated solutions.\*

A considerable number of compounds, both organic and inorganic, have been recommended as stabilizers to be added in small amounts to hydrogen peroxide solutions, and a number of investigations of their comparative effectivenesses have been reported (3, 7). These studies are discussed in a later section.

Solutions of 85 - 90% hydrogen peroxide are not sensitive to agitation or to mechanical shock--even bullets shot through the solution have failed to detonate it.\*\*

It is common knowledge that the decomposition rate of hydrogen peroxide is markedly increased by the presence of minute concentrations of certain catalytic ions, particularly of the metals the ions of which can exist in more than one oxidation state--such as  $\text{Fe}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cr}^{+++}$ --or by suspended

\* For example, Giguère and Geoffrion (2) observed that when 90% unstabilized hydrogen peroxide was diluted with redistilled water the solutions so obtained invariably showed a marked tendency to decompose, so that a small quantity of sodium stannate had to be added in order that measurements of refractive index of the solutions could be carried out.

\*\* The explosive characteristics of peroxide solutions and of vapors containing hydrogen peroxide are considered in Chapter 4.

or colloidally dispersed catalytic matter, or by the walls of the container if they contain catalytically active substances. This latter heterogeneous decomposition process may even be induced by rough surfaces or the presence of minute scratches on the inner walls of a glass container. At times streams of minute oxygen bubbles may be observed to issue from a tiny point on the surface of the container, which even under the microscope reveals no irregularity or difference in appearance from the rest of the surface. Horkheimer (4) studied the stability of dilute hydrogen peroxide solutions in glass vessels and concluded that the nature of the distilled water employed and the quality of the glass container were chiefly responsible for the observed results, and that with glass of the "highest purity" no preservative was required, especially at lower temperatures near 16 to 18° C. In this connection, the stability of dilute hydrogen peroxide when stored in ordinary glass bottles, in brown glass bottles, or in glass bottles coated internally with paraffin, was studied at room temperature by Ivanov and Dochikjan (5), among others. These investigators found that the concentration of the peroxides decreased in a 4-months' period from an original 2.93% to 0.02% in clear glass, to 0.48% in brown glass and to 2.71% in paraffin-lined glass, either clear or brown. The alkalinity imparted to the solution by common soda glass, together with any roughness of the glass surfaces, is doubtless responsible for the nearly complete decomposition shown by the samples in the uncoated glass vessels.

Paraffining of the glass surface, however, is not a completely satisfactory preventive for decomposition of peroxide, especially at higher concentrations (6). For storage of hydrogen peroxide at ordinary temperatures, the use of paraffined glass has largely been superseded by bottles of polyethylene plastic, which is well suited for this purpose.

4.

## DETERMINATION OF THE STABILITY OF HYDROGEN PEROXIDE SOLUTIONS

### Direct Analysis of Hydrogen Peroxide Sample

The simplest method of determining the rate of decomposition of a concentrated solution of hydrogen peroxide at a given temperature is to analyze the solution, as by titration with a standard acid solution of potassium permanganate, at the beginning and end of a measured interval of time. The reaction involved in the analysis, as pointed out in Chapter 10, is indicated by the equation:



This method gives satisfactory results, especially in long-range storage tests at room temperature, in which the rate of decomposition may be very low, or in tests where large changes in concentration occur. In either of these cases, the gas evolution method described below may be impractical. For precise data, attention must be given to such errors as temperature variation and the loss of hydrogen peroxide and particularly water from the solution by evaporation. For example, in tests at substantially elevated temperatures it is desirable to surmount the sample vessel with a simple air or water-cooled condenser to retain water and hydrogen peroxide which would otherwise be carried away in the vapor form with the oxygen evolved. It is also possible for a sample to gain water from the surrounding air if the latter is sufficiently moist and the hydrogen peroxide is highly concentrated. For further details of the analytical procedures applicable to the determination of hydrogen peroxide, see Chapter 10.

### Gas Evolution Method

Another method of measuring the decomposition rate of hydrogen peroxide which has proved to be convenient and reliable, especially for laboratory testing, is the gasometric or gas evolution method, carried out at a temperature selected so as to provide a satisfactory volume of oxygen gas formed in

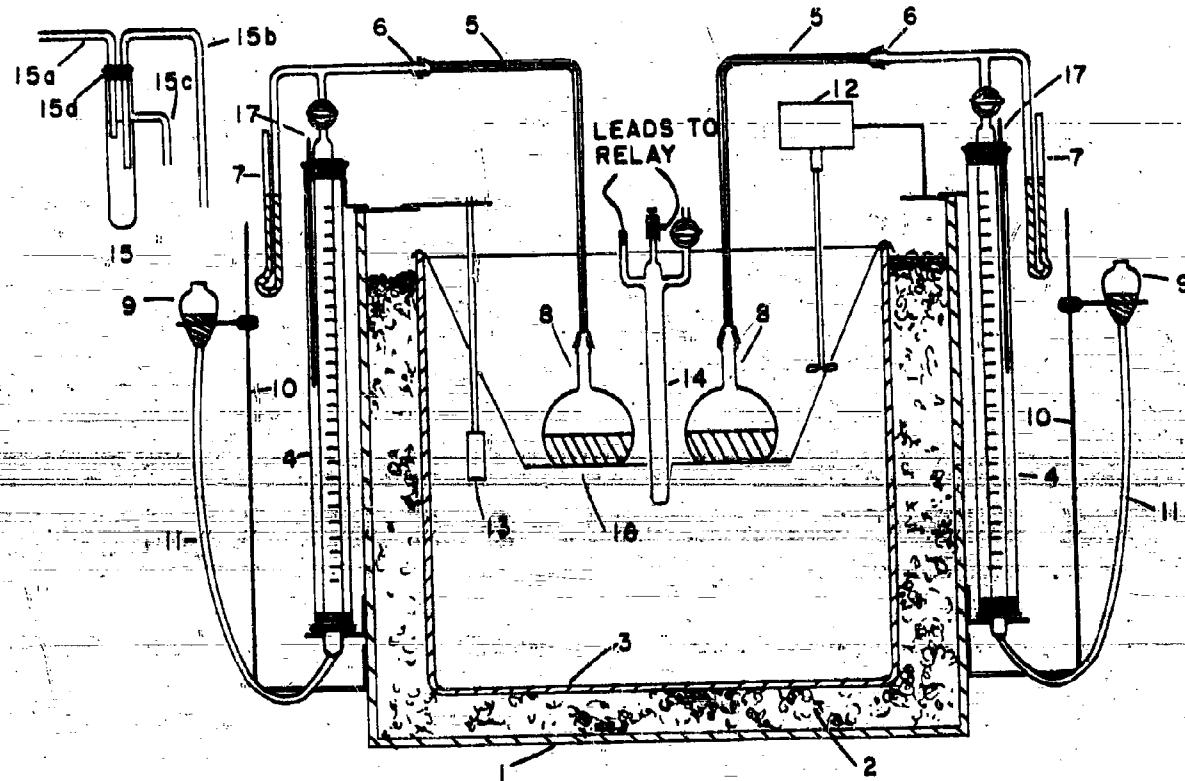
a convenient time interval by the decomposition reaction:

$2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$ . The apparatus (7) employed is represented in Figure 1. The oxygen is collected in a gas buret over mercury\* and from its volume, corrected to standard conditions, the amount of decomposition suffered by the sample of hydrogen peroxide may be calculated. The decomposition rate, so determined, may be expressed in several ways; frequently the percent of the hydrogen peroxide originally present in the solution which has been decomposed per hour (or day or year) at a known temperature is calculated. Thus a high grade, unstabilized 90 wt. % hydrogen peroxide solution may show a decomposition rate at 50°C. of about 0.0010 percent per hour, by which statement it is implied that 0.001% of the number of molecules of  $\text{H}_2\text{O}_2$  originally present is decomposing per hour. If the rate is sufficiently small the quantity of peroxide may be considered as essentially unchanged over the period of measurement. In the same way, on this basis a decline in concentration at the rate of 1 percent per hour in the content of hydrogen peroxide in an originally 50 wt. % solution would lead in 1 hour to a solution of 49.5%  $\text{H}_2\text{O}_2$ , and not to 49.0%  $\text{H}_2\text{O}_2$ . Alternatively, the number of cc. of oxygen gas (expressed at standard pressure and temperature) evolved per gram or per cc. of the solution during a specified time, such as 24 or 48 hours, at a specified temperature, usually 50°, 55°, 60°, or 100°C., may be used to express the rate of decomposition of the hydrogen peroxide.

It is worthy of note that the graphical representation of decomposition rate data for different hydrogen peroxide con-

\* About a milliliter of water may be conveniently placed above the mercury in the buret, so as to permit the gas collected to become saturated with moisture at the temperature of measurement. For low decomposition rates a microburet (preferably water-jacketed) is required and capillary Pyrex tubing connects the sample container (placed in a thermostat at the desired temperature) with the buret. Measurements are usually taken only after from four to sixteen hours' standing, in order that supersaturation effects may be relieved and so that consistent results may be obtained in successive determinations.

6.



1. WOODEN BOX	8. 250 ml. FLASK WITH 14/35 T GROUND GLASS JOINT	15. CONSTANT LEVELLING DEVICE FOR BATH
2. GLASS WOOL	9. MERCURY LEVELING BULB	15a TAP WATER INLET
3. PYREX JAR - 12" DIAMETER	10. STEEL ROD FOR SUPPORT OF LEVELING BULB	15b WATER INLET TO BATH
4. 10 ml. MICRO BURET WITH WATER JACKET	11. RUBBER TUBING	15c OVERFLOW
5. PYREX CAPILLARY TUBING	12. STIRRER MOTOR	15d RUBBER STOPPER WITH VENT
6. 10/30 T GROUND GLASS JOINTS	13. PLUNGER TYPE HEATER	16. PERFORATED COPPER PLATE FOR SUPPORT OF FLASKS
7. MANOMETER	14. MERCURY REGULATOR	17. THERMOMETER (0-100°C)

FIGURE 1 - APPARATUS FOR DETERMINATION OF DECOMPOSITION RATE BY GAS EVOLUTION METHOD

centrations by these two alternative methods may lead to curves of different forms. Thus when decomposition rate is plotted against concentration of hydrogen peroxide the second method leads to a curve with a flat maximum, which is lacking in the plot obtained by the first method (7). (See Figure 2.)

#### Discussion of Methods for Determining Stability

If the decomposition rate of the hydrogen peroxide solution is of the order of 0.1% per hour at 50°C., or greater, the gas evolution method becomes impracticable, mainly because the volume of gas to be measured increases too rapidly to be measured conveniently. In this case, also, the concentration of the hydrogen peroxide solution no longer can be considered to remain unchanged over the period of measurement, as may safely be assumed to be the case at low decomposition rates.

In cases where low decomposition rates are expected, the choice of a somewhat higher temperature for the thermostatic bath may be advisable in order that the volume of oxygen collected in a reasonable period of time may not be too small to be measured with accuracy. For hydrogen peroxide samples of average stability, temperatures of 50°C. or 60°C. are convenient. For industrial research purposes an accelerated test at 100°C. for 24 hours has been much employed, but the constancy and reproducibility of measurements carried out at so high a temperature may be found to be somewhat inferior to those obtainable at lower temperatures.\*

Since even under favorable circumstances reproducibility of measurements carried out in different flasks is sometimes difficult to attain, due to the capricious character of some of the

\* German investigators frequently reported a "Z number" (Zersetzungszahl), which was the percentage of the peroxide decomposed in a 24-hour period at 96°C. It is probable that this temperature represented that provided by a steam-bath under prevailing laboratory conditions. The change in the percentage composition of the peroxide solution in this case was determined by titration of samples with permanganate solution at the beginning and at the end of the test period.

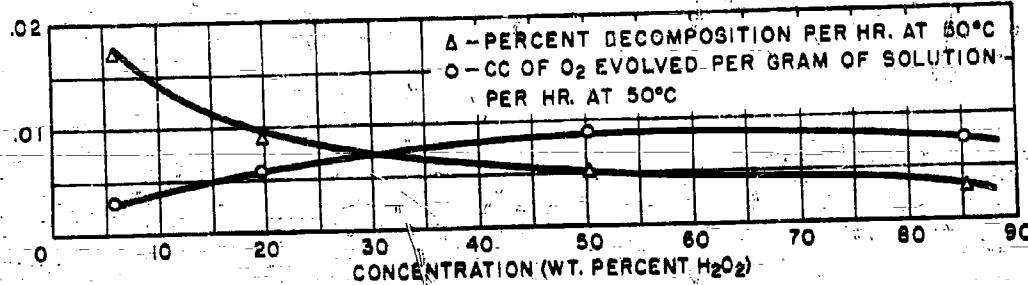


FIGURE 2 - ALTERNATIVE METHODS OF REPRESENTING DATA ON  
DECOMPOSITION OF HYDROGEN PEROXIDE

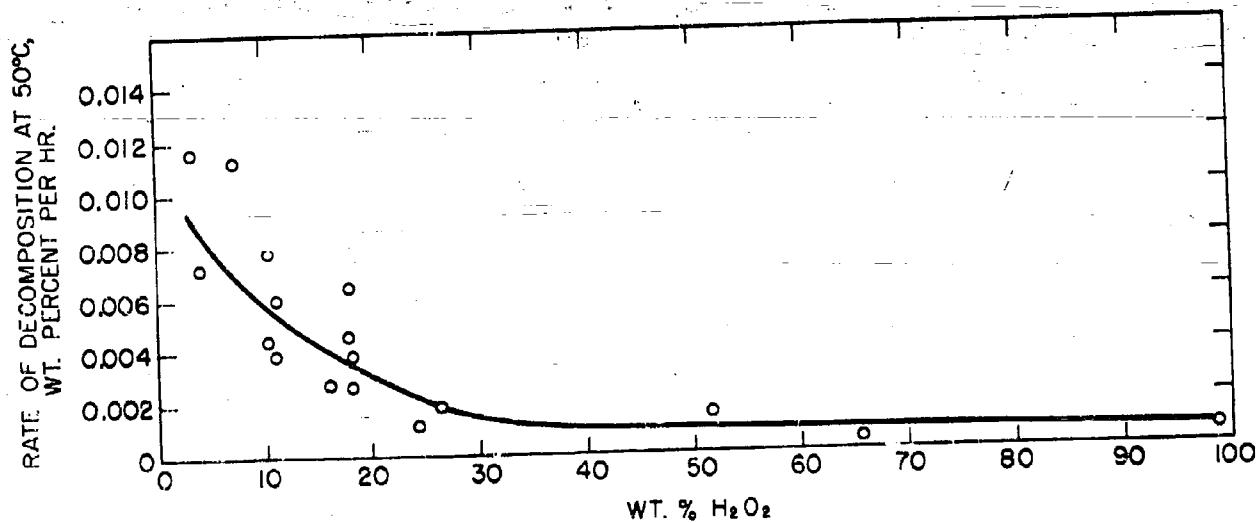


FIGURE 3-RATE OF DECOMPOSITION OF H<sub>2</sub>O<sub>2</sub> AT 50°C AS A FUNCTION OF CONCENTRATION

errors which may be encountered, it is essential that a sufficient number of duplicate samples be employed in carrying out measurements of decomposition rate to furnish reliable average values.

As carried out under usual laboratory conditions the effect of diffuse daylight upon the decomposition rate of hydrogen peroxide solutions is small enough to introduce no significant error into the results obtained. If comparative measurements are to be carried out under conditions of illumination which are variable in intensity or frequency, this situation may introduce an appreciable source of error, especially if frequencies in the ultraviolet range are involved in some of the experiments. Provision has been made in some cases for carrying out the measurements with complete exclusion of light.\* The results of measurements of the rate of decomposition of unstabilized hydrogen peroxide solutions at 50°C. as a function of concentration, are shown graphically in Figure 3.

As above indicated, where the decomposition rate is too high to be measured accurately by the gas evolution method, the titration method may still be employed. For example, starting with a sample of known weight and concentration of hydrogen peroxide, held at a constant temperature, portions may be withdrawn after measured intervals of time, rapidly weighed, and then immediately frozen in a Dry Ice-acetone bath so as to reduce the decomposition rate to a negligibly small value. The test portions may then be transferred individually to a volumetric flask, and after making up to the mark, portions of the diluted solution may be taken for titration with standard permanganate solution in the presence of sulfuric acid. From these data the loss of active oxygen may be calculated.

Alternatively, the original sample may be divided among a number of small Pyrex or quartz tubes (each containing, for example, about 1 ml. of solution, accurately weighed), provided with

\* The protective action of colored glass vessels as containers for dilute and concentrated hydrogen peroxide has been discussed by Buchi and Kurer (8).

10.

ground-glass caps and capillary vent tubes. The tubes are withdrawn at various times, one by one, from the constant temperature bath. Each is chilled and the hydrogen peroxide content determined by titration as before. Knowing the quantity of hydrogen peroxide present in the original sample, and assuming that the initial decomposition rate in each of the small tubes was identical, the titration data make possible the calculation of the rate constant for the decomposition reaction under the conditions of the experiment.

Another technique is to contain the sample in a small tube provided with a cap having a terminal length of capillary. This acts as an air-condenser to remove water or possibly also hydrogen peroxide vapor which would otherwise escape with the oxygen evolved. Therefore it may be feasible to determine the amount of oxygen evolved by accurate weighing of the sample tube plus cap before and after the experiment, from which the rate of hydrogen peroxide decomposition can be calculated.

Where the decomposition is conveniently slow, the gas evolution method may also be modified so as to observe the change in pressure of the oxygen produced at constant gas volume. In this case a manometer takes the place of the gas buret and a leveling device is used to bring the confining liquid in the manometer always to the same point in the arm directly attached to the sample tube. Experience with this arrangement has revealed little advantage over the more conventional, constant pressure method; and at higher decomposition rates it likewise becomes impracticable.

The gasometric determination of the decomposition rate of hydrogen peroxids lends itself to a certain degree of instrumental automatic control, to lessen the number of manual and visual operations required, especially where a large number of determinations is required. Such instrumentation, however, is hardly justified unless a routine program of considerable magnitude and duration is involved.

Other attempts to simplify the determination of the hydrogen peroxide content of aqueous solutions have involved the measurement of physical properties, such as the refractive index and the density of such solutions. If the solution is known to contain essentially nothing but hydrogen peroxide and water, and if the temperature of the solution is carefully controlled, accurate measurement of the refractive index or of the density of the solution may be used as a method of determining the concentration of the peroxide (9).

#### EFFECT ON STABILITY OF SURFACE-TO-VOLUME RATIO AND NATURE OF SURFACES

##### Surface-to-Volume Ratio

Experiments carried out in Pyrex glass vessels on a laboratory scale at 50°C. have shown that the decomposition rate of pure hydrogen peroxide solutions under these conditions is roughly proportional to the ratio of surface to volume over a considerable range; i.e., the heterogeneous decomposition reaction on the walls of the container is usually far faster than the homogeneous decomposition, in laboratory-size vessels.

In Figure 4, which represents the results of experiments carried out on unstabilized, 90% hydrogen peroxide, under conditions permitting a six-fold variation in the surface-to-volume ratio, it is clear that, whereas the curve is roughly linear in the higher ranges of s/v, it flattens out at lower ratios to an approximately constant value, approaching 0.001 percent per hour at 50°C. In the ideal case, where no dissolved or solid catalysts were present, this lower limit should represent the value of the homogeneous decomposition reaction rate of a pure hydrogen peroxide solution, below which it cannot be hoped to go at the temperature specified. There is reason to believe that under conditions for which the s/v ratio is small (as in a large storage tank), this limiting value approaches zero. In any actual case, where some heterogeneous catalytic activity is to be expected, the minimum value will exceed the true homogeneous reaction

DECOMPOSITION RATE, WT.% PER HR. AT 50°C

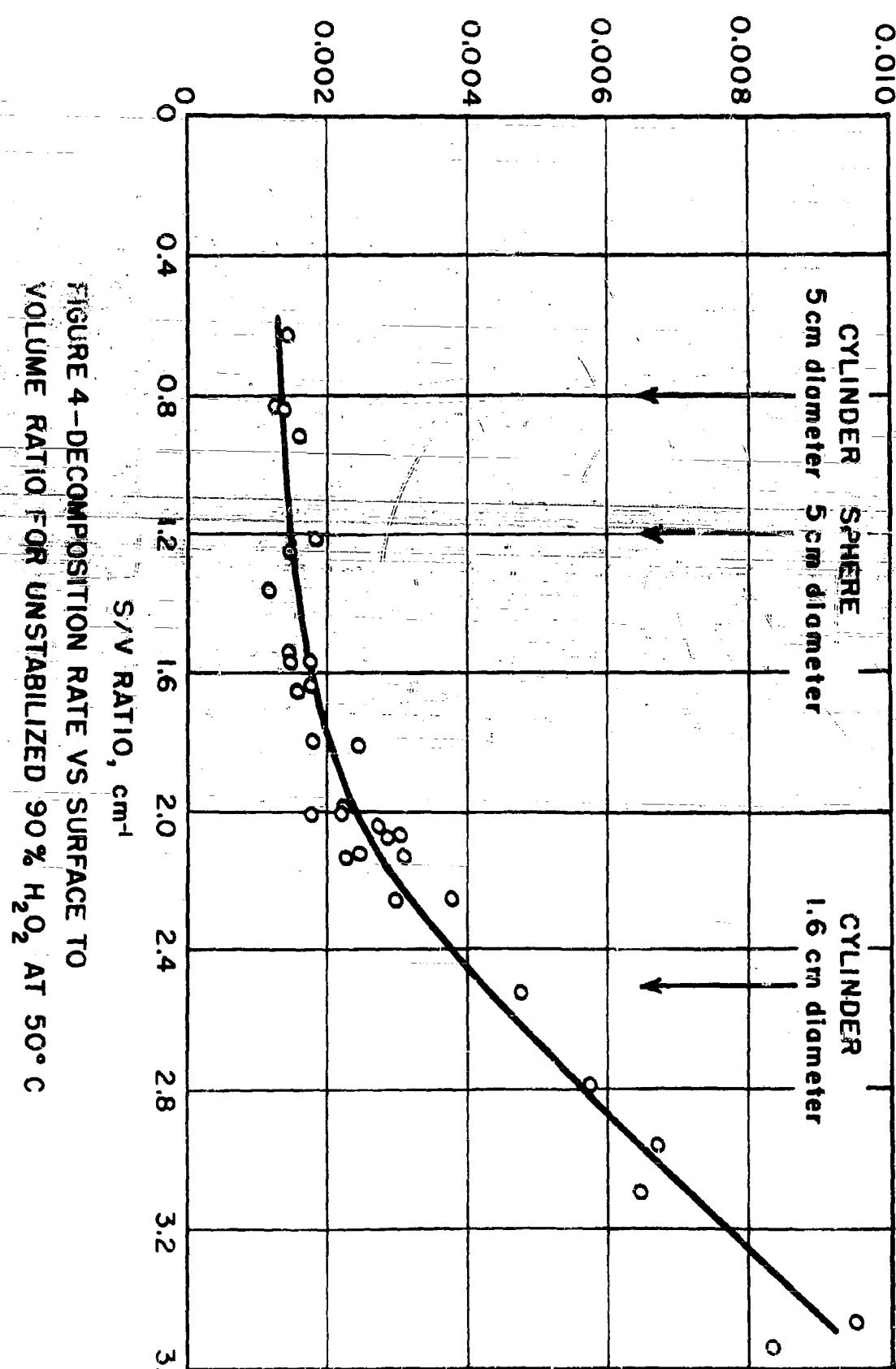


FIGURE 4-DECOMPOSITION RATE VS SURFACE TO VOLUME RATIO FOR UNSTABILIZED 90% H<sub>2</sub>O<sub>2</sub> AT 50° C

rate.\* The curve as a whole would be displaced downward in the presence of stabilizers; as previously indicated, minimum decomposition rates at 50°C at least as low as 0.0003 percent per hr. have been observed. These represent more closely the actual value of the homogeneous decomposition rate for a pure hydrogen peroxide solution (90%) at this temperature. In the case of the curve shown, small amounts of catalytic impurities picked up in the laboratory handling of the samples were no doubt responsible for a minimum reading as large as 0.001% per hr.

In the ideal case of complete purity of the solutions, it is not unreasonable to expect that the intersection of the curve with the ordinate axis may come close to the origin.

#### The Surface of Storage Containers

Common soda glass containers release a sufficient amount of alkali to hydrogen peroxide solutions contained therein to render them quite unsuitable for storage purposes unless stabilizers are added. When the heterogeneous decomposition reaction has been eliminated as far as possible, there remains the homogeneous decomposition reaction, the rate of which, as stated, is known to be exceedingly low at ordinary temperatures for the purest obtainable samples, but is very sensitive to the effect of various catalytic dissolved substances, and to the acidity or alkalinity of the solution.\*\*

\* It is of interest to locate on Figure 4 the values of the abscissa which correspond approximately to some common laboratory vessels in which stability measurements are made. The ratio of surface to volume for a sphere of radius  $r$  is equal to  $3/r$ , and for a circular cylinder is  $2/r$  (if the area of the ends is neglected). The figure locates  $s/v$  values corresponding to circular cylinders of 1.6 cm (test tube) and 5 cm. (beaker) in diameter, and a 5 cm. diameter sphere (flask).

\*\* At least as early as 1894 it was pointed out by Wolffenstein (10) that a solution of hydrogen peroxide, free from alkali or traces of heavy metal compounds, possesses a considerable degree of stability and that it may be distilled and concentrated without appreciable loss by decomposition. This stability of pure hydrogen peroxide was appreciated by still earlier workers, as far back as Thenard.

Pyrex glass has been found suitable as a container material, after a thorough cleansing with concentrated nitric acid, followed by rinsing and leaching with hot conductivity water. Pure metallic aluminum, tin, magnesium, or certain magnesium-aluminum alloys, and certain stainless steels have a minimum catalytic effect on the decomposition process, and are of interest as materials of construction for storage tanks for hydrogen peroxides (see Chapter 4).

In the case of metallic aluminum, the effect of impurities in the metal may be seen in the fact that the rate of decomposition of 70% hydrogen peroxide at 30°C. was doubled when 99.0% aluminum was substituted for the pure metal as the container. As little as half of 1 percent of impurities in the metal causes a distinct rise in the decomposition rate of hydrogen peroxide. The process of anodizing the aluminum, resulting in a more perfect coating of the surface with aluminum oxide, followed by heating with water to seal the pores, results in an improvement in the behavior of the metal as a container for hydrogen peroxide solutions. However, this process is not conveniently applicable to the conditioning of large-scale storage tanks. A satisfactory condition of the aluminum inner surface of large storage tanks may be attained by filling the container with 1:1 concentrated nitric acid (sometimes preceded with a preliminary soaking in caustic soda solution), whereby the metal is "passivated" through the formation of an adherent oxide film.

On a smaller scale, certain plastics, such as polyethylene, also have been employed for storage. When used alone, such containers have shown satisfactory performance at room temperature. At temperatures appreciably higher than this diffusion of the liquid through the plastic may render this material unsuitable for the purpose.

Coatings of various resistant substances have been applied to the walls of metal containers, but the danger here lies in the possibility of pores or fissures in the coating, with the resulting danger of contact of the hydrogen peroxide

with the underlying metal. Decomposition of the hydrogen peroxide then causes the coating to be stripped off. Even a continuous plastic coating is unsatisfactory, since it may be permeable to hydrogen peroxide diffusion, and may slowly become stripped off by the same mechanism.

The importance of the surface condition of the containing vessel, in its effect upon the stability of hydrogen peroxide solutions contained therein, can be seen not only in the fact that under most circumstances the heterogeneous decomposition of the peroxide is responsible in very large part for the extent of decomposition observed, but also by the ability of certain metals, otherwise catalytically active, to assume an inactive or passive state toward hydrogen peroxide solution when suitably conditioned.

In this connection, metallic iron, which has been passivated by immersion in concentrated nitric acid, and then cautiously rinsed with distilled water, causes no visible decomposition of even 90% hydrogen peroxide when lowered into the peroxide solution. However, once the passive coating has been abraded at a given spot, activity is rapidly restored over the entire surface, so that contact with concentrated hydrogen peroxide solution is no longer possible without immediate vigorous decomposition of the hydrogen peroxide.

In a similar fashion, passivation of the iron by immersion in a dilute solution of a soluble bichromate, followed by careful rinsing, brings about passivation of the iron, so that it fails to affect noticeably the decomposition rate of hydrogen peroxide with which it may have been brought into contact, even after many hours. Abrasion of the surface film of the iron, passivated by this means, renders active only that part of the surface which has been scratched through--the remaining surface maintaining its passive condition. It may be inferred from this result that the chemisorbed chromate groups covering the surface of the passivated metal are oriented in such a manner as to present to the solution an essentially continuous layer of oxygen atoms, which screen the underlying chromium from direct contact with the hydrogen peroxide solution.

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Further aspects of the compatibility of hydrogen peroxide solutions with various materials of construction are considered in Chapter 4.

#### STABILITY OF CONCENTRATED HYDROGEN PEROXIDE

In considering the available stability data on very concentrated solutions of hydrogen peroxide, it is of interest to recall the careful quantitative studies of various physical properties of such solutions, as well as of pure hydrogen peroxide carried out by Maass and co-workers (11) which were possible only because of the high degree of stability of this substance in the absence of contaminants. Regnault and LeNoir de Carlan (12) also prepared hydrogen peroxide of a sufficient degree of stability to attain nearly 100% concentration by evaporation of commercial "100 to 130-volume" material to about 60% hydrogen peroxide, followed by fractional distillation in Pyrex apparatus.

More recently Shanley and Greenspan (1) reported the following data on the rates of decomposition of 90% unstabilized hydrogen peroxide at temperatures ranging from 30° to 140°C.: at 30°, 1% per year; at 66°, 1% per week; at 100°, 2% per hour; at 140°, rapid decomposition with boiling. They pointed out that no attainable pressure has any noticeable effect upon the rate of decomposition, and that probably the only additive which actually decreases the rate of decomposition in the homogeneous uncatalyzed reaction is the hydrogen ion, as indicated in the equation:  
 $\text{HOOH} \longrightarrow \text{H}^+ + \text{OOH}^-$ , for which the equilibrium constant was given by Evans and Uri (3) as  $K = 2.24 \times 10^{-12}$  at 25°C. There is some reason to question the complete validity of this interpretation of the effect of hydrogen ion, as will be made evident by the discussion presented in a later section (p. 34). However, this interpretation of the effect of added hydrogen ion is in line with the assumption that addition of stabilizers in general serves to nullify the influence of catalysts which may be present in the solution, since it is well known that in the presence of an excess of OH<sup>-</sup> ion the stability of hydrogen peroxide declines rapidly.

### EFFECTS OF CATALYTIC IMPURITIES ON STABILITY

The effects of the addition of small proportions of various metal ions are shown in Table 1.

TABLE 1  
EFFECT OF ADDED IONS ON THE DECOMPOSITION RATE  
OF CONCENTRATED HYDROGEN PEROXIDE,  
FROM SHANLEY AND GREENSPAN. (1)

Added Ion	Amount Added, mg./l	% Original Active O Lost in 24 hr. at 100°C.
None	---	2
Al <sup>+++</sup>	10.	2
Tin <sup>++</sup>	10.	2
Zn <sup>++</sup>	10.	10
Pt <sup>++</sup>	1.0	15
Cu <sup>++</sup>	0.01	24
Cu <sup>+</sup>	0.1	85
Cr <sup>+++</sup>	0.1	96

The effect of variation of the quantity of catalyst present (for example, cupric ion in Table 1) upon the rate of decomposition of a fixed amount of hydrogen peroxide is, as would be expected, to bring about an increase in the rate of decomposition as the concentration of catalyst is increased.

As a rule, metals are less active catalysts than their oxides. For example, bright copper may have an inappreciable effect upon the stability of concentrated solutions of hydrogen peroxide for a time, but as soon as its surface acquires a minimal coating of oxide, a rapidly increasing rate of decomposition is observed. Oxides of certain metals are among the commonest decomposition catalysts for hydrogen peroxide. Oxides such as  $\text{Ag}_2\text{O}$ ,  $\text{MnO}_2$ ,  $\text{PbO}$ , and  $\text{Pb}_3\text{O}_4$  react intensely with concentrated hydrogen peroxide. Oxides of certain other metals, such as aluminum, tin, zinc, or cadmium, have no appreciable catalytic effect upon the rate of decomposition of hydrogen peroxide, and may indeed serve as stabilizing agents. It is obvious that the fineness of division

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of the solid particles and the consequent surface exposed have a controlling influence upon the observed reaction rate, as have the purity and the surface configuration of the solid. (Catalytic decomposition of hydrogen peroxide is considered in more detail in Chapter 8.)

In addition to the temperature and concentration of the solution of hydrogen peroxide and the presence of catalytic impurities, other factors as previously indicated, bear upon the observed rate of decomposition, including the pH of the solution—considered in greater detail below; the wall effect of the containing vessel, including the surface-to-volume ratio; and the effect of radiant energy, such as ultraviolet light. When samples of 90% unstabilized hydrogen peroxide, contained in glass vessels, are illuminated by direct sunlight, they may undergo decomposition to the extent of about 1% per day at room temperature; and proportionally higher percentage decomposition is possible by exposure to more intense illumination. Conceivably an effect of agitation of the solution also might be anticipated, but over a wide range no such effect has been noted. Shaking a solution of hydrogen peroxide may cause bubbling to occur, due to the release of supersaturation with oxygen; but this result is not due to an increase in the decomposition rate of the hydrogen peroxide.

In this connection it should be pointed out that, although 100% pure hydrogen peroxide, free of all admixtures, has been described as sufficiently stable at ordinary temperatures as to resist shock and projectiles, mixtures with fuels, such as alcohols, may be explosive.\*

#### Mixed Catalysts

An interesting aspect of the catalytic decomposition of hydrogen peroxide is concerned with the effect of mixed catalysts. In the case of solid catalysts containing certain mix-

\* For further details on the explosive characteristics of hydrogen peroxide see Chapter 4.

tures of co-precipitated hydroxides, it has been observed that the effect of the mixture was in some cases much greater than the sum of the effects of the oxides when applied separately. Likewise, if to a sample of 90% unstabilized hydrogen peroxide a ferric salt solution is added, equivalent in the final solution to 0.1 p.p.m.  $\text{Fe}^{+++}$ , and if, similarly, addition is made of a cupric salt supplying 0.1 p.p.m. of  $\text{Cu}^{++}$ , the observed rate of decomposition of the peroxide at some fixed temperature will be found to greatly exceed the combined rates of decomposition of the same hydrogen peroxide solution when singly catalyzed with the respective contaminants under like conditions. This behavior is shown in Figure 5. Other pairs of catalytic agents may show similar results, but the effect is not invariably observed; as, for example, in the case of the addition of a mixture of salts supplying ferric and silver ions, where no additional increase in the rate of decomposition, above the sum of the separate effects, was observed.

In a study of the catalytic effect of various simple metal cations upon the decomposition of hydrogen peroxide, Uri (15) observed that the presence of chloride ion with these metal cations resulted in an increase in the rate of decomposition to about forty times the original value. In this case the promotional effect is therefore brought about by addition of an anion, rather than a second cation. The interpretation suggested by Uri assumes the mechanism to be of the free radical chain type.

#### Periodic Catalytic Decomposition

It is also noteworthy that the catalytic decomposition of hydrogen peroxide in moderately dilute solution (of the order of 1 to 10 wt. % hydrogen peroxide), and within a certain range of pH, in the presence of mercury, is subject to a remarkable periodicity, resulting in a rhythmic, pulsating evolution of oxygen alternating with periods of practical cessation of gas evolution. The first observations, reported by Bredig and Weinmayr (16), were made upon a 1% hydrogen peroxide solution kept in contact with mercury, samples being titrated at regular intervals with potassium

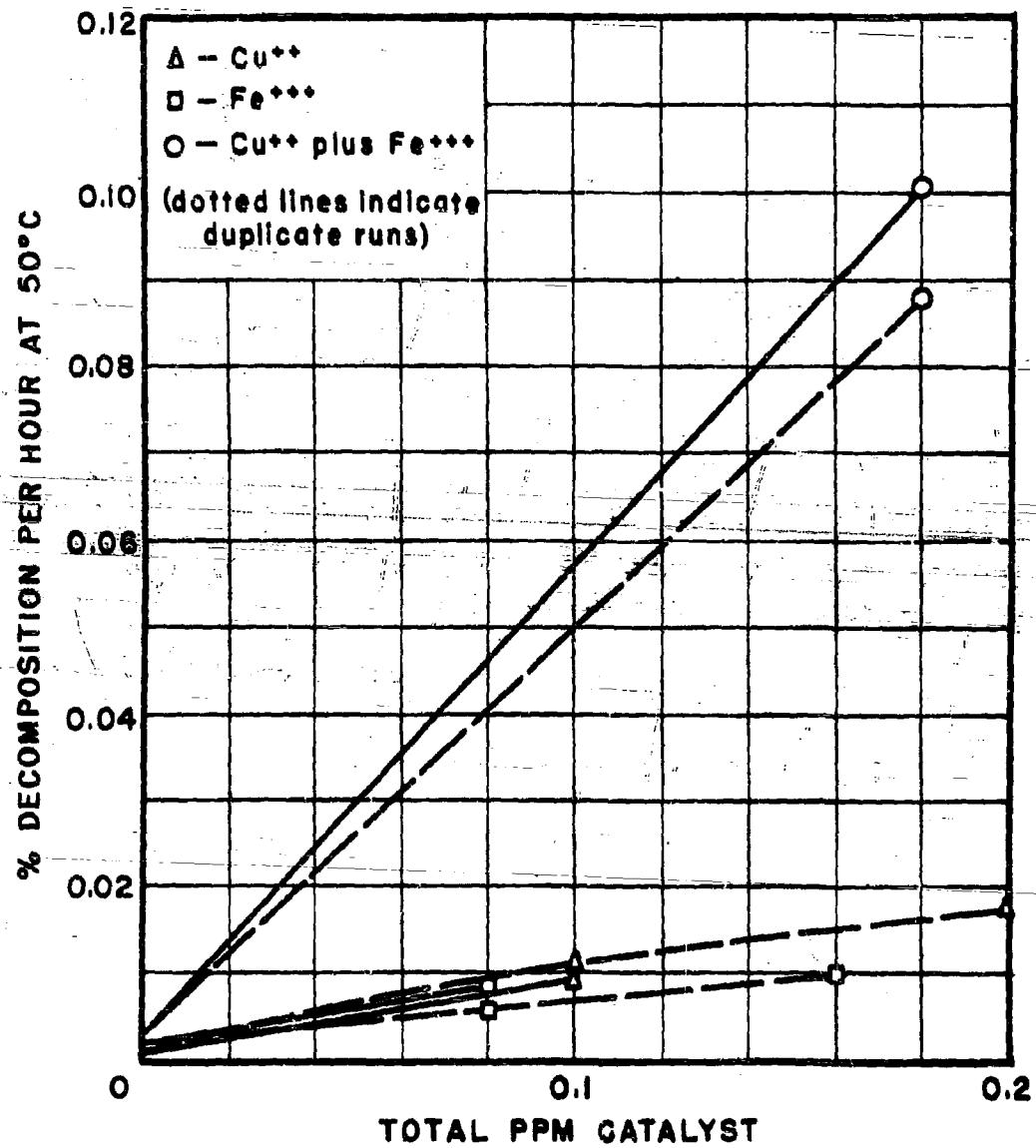
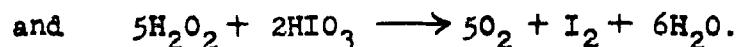


FIGURE 5 - EFFECT OF MIXED CATALYST ON  
DECOMPOSITION RATE OF 90% HYDROGEN PEROXIDE

permanganate. The titration curve indicated a periodic decomposition of the hydrogen peroxide. A simple observation of this phenomenon is possible by covering about 1 ml. of mercury in a tube with about 10 ml. of 10% hydrogen peroxide. Under favorable conditions the periodic evolution of clouds of small bubbles of oxygen is strikingly evident. However, the presence or absence of minute quantities of other substances may have an important effect upon the appearance of the periodic effect. Thus, addition of alkali to the extent of 0.0001 to 0.001 M in concentration was found to be most favorable, while sodium chloride at a dilution of  $2 \times 10^{-6}$  N had an inhibitive effect. If carried out in common soft glass vessels, a sufficient degree of alkalinity may be attained by allowing the solution to stand therein for several hours prior to the onset of the pulsations.

Van Antropoff (17) and Fredenhagen (18) studied the periodic catalysis in greater detail and concluded that the formation of an oxide film, periodically covering the mercury surface and alternately redissolving, was responsible for the phenomenon, which is also described by Hedges and Myers (19) in a monograph devoted to physico-chemical periodicity of various types. These authors describe other cases of catalysis of the decomposition of hydrogen peroxide which under suitable conditions may exhibit periodicity. Among these is the interesting case of periodicity in a homogeneous system, as reported by Bray (20), who studied the decomposition of hydrogen peroxide by iodine. The decomposition reaction is catalyzed by iodine and iodic acid, which enter into such reactions as are indicated in the following equations:



In the presence of certain concentrations of sulfuric acid the solution is observed to become periodically darkened by the setting free of iodine, and oxygen slowly diffuses out of the solution. Although this case is reported as one of the few instances of periodicity observed in a homogeneous solution, it is also possible

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that the process may be subject to control by surface conditions, such as arise from the part played by the walls of the containing vessel.

#### EFFECT OF TEMPERATURE UPON STABILITY

As a result of measurements of decomposition rates of highly pure, unstabilized hydrogen peroxide solutions at temperatures varying from 50° to 70°C., the temperature coefficient, a, for the decomposition reaction was found to be  $2.2 \pm 0.1$  for a 10-degree rise. The coefficient appears in the expression  $k_2 = k_{T_1} a (T - T_1)/10$ , where  $k$  is the reaction rate constant at the temperature  $T$  or  $T_1$ . This value agrees well with that calculated from results of other measurements (21), carried out on hydrogen peroxide solutions at 96°C. over the entire possible range of concentration. From these measurements a ratio of about 40:1 was indicated between the decomposition rate at 96°C. as compared to the 50°C. value. The ratio calculated by the use of the equation given above is approximately 38:1.

In the presence of catalytic contaminants it would be expected that the temperature coefficient should be less than 2.2; and indeed this belief has been borne out by measurements of the temperature coefficient of the decomposition reaction in the presence of small proportions of ferric salts added to the solution. For such solutions values of a as low as 1.6 were observed. On the other hand, in the presence of a stannate stabilizer, the coefficient never fell below 2.2, sometimes rising slightly above this value, to 2.3 or 2.4. Although no high degree of accuracy is claimed for these determinations, it seems justifiable to assume that the effects reported are real.

#### STABILIZING AGENTS

Although it appears reasonably certain that in the presence of more than minute proportions of catalytically-active contaminants it is impossible to restrain the decomposition of hydrogen peroxide by the addition of stabilizers much effort

nevertheless has gone into the study of the stabilization of hydrogen peroxide with the hope of improving the storage characteristics of commercial products.

#### General Principles of Stabilization

When viewed in its broadest aspects, the stabilization process--aside from control of the pH of the peroxide solution, which would influence the rate of the homogeneous decomposition reaction--may be assumed to consist of inactivating catalytically-active substances which may be present, either dissolved or suspended in the solution, or held in the walls of the container. The validity of this assumption is attested by the fact that the addition of stabilizing agents to concentrated hydrogen peroxide solutions of exceptionally high purity fails to reduce further the rate of decomposition of the peroxide solution to any important degree. That repression of the ionization of hydrogen peroxide by addition of acids, such as sulfuric, phosphoric or pyrophosphoric, oxalic, or benzoic acids, cannot solely account for the improvement of the stability of hydrogen peroxide solutions is indicated by the fact that some other acids have less effect when so employed than would be anticipated from a knowledge of their acid strengths. Furthermore, if enough acid were added to reduce the pH to values of 2 or less (measured at ten-fold dilution), the effect of the addition would be to decrease the stability of the peroxide. It has been suggested that conceivably the ability of the acid to enter into compound formation with hydrogen peroxide may also have some bearing upon its effectiveness.

Organic substances in general are subject to a slow oxidation at ordinary temperatures by hydrogen peroxide. Therefore for long-term storage the use of organic acids, for example, uric, citric, tannic, or salicylic acids, as stabilizers may not prove to be adequate, particularly for higher concentrations of hydrogen peroxide. For some purposes, as in medicinal uses, the organic acids are nevertheless preferred in dilute peroxide solutions to stronger inorganic substances which might have injurious effects. It should furthermore be borne in mind, as pointed out by Tritton (22)

that when hydrogen peroxide is to be used for pharmaceutical purposes, the presence of substances which affect the decomposition of hydrogen peroxide by catalase may become a matter of importance.

A very extensive number of stabilizers, both inorganic and organic in character, have been tested with hydrogen peroxide solutions, both dilute and concentrated. Among these substances the most notable success appears to have been obtained, especially in the case of the highly concentrated solutions, with sodium stannate or with 8-hydroxyquinoline ("oxine"), each in the presence of a soluble pyrophosphate, or a phosphate-pyrophosphate mixture. Since the part played by many catalysts is believed to depend upon their ability to enter into a cycle of reactions, in which oxidation and reduction of a constituent occurs in rapid alternation, it follows that one way in which stabilization may occur is by terminating or breaking the reaction chain in such a case. If the catalytic source is located in the walls of the container, the stabilizer may serve to alter the character of the surface so that it will no longer aid in the decomposition process. Some colloidal stabilizers, such as hydrous stannic oxide, are effective in adsorbing catalytically-active ions or in bringing about coagulation of dispersed active solid matter. Thus, it is common practice, as previously indicated (2), to add at least a few p.p.m. of sodium stannate to highly concentrated hydrogen peroxide, otherwise free of additives, in order to improve the stability characteristics of these solutions. Similarly, addition of sodium pyroantimonate to concentrated hydrogen peroxide solutions brings about a smaller, but measurable increase in the stability of the solution, due doubtless to the presence of colloidal hydrous antimony pentoxide.

The addition of sodium pyrophosphate (0.15% or less), as suggested by Reichert and others is believed to improve the stabilizing effect of colloid stannic oxide (23a.), due in part to the fact that the precipitation of the tin is thereby retarded.

Industrial application has been made of stabilizers which exist in colloidal form in hydrogen peroxide solutions employed in

bleaching cotton and other textiles. Addition of sodium or magnesium silicate to alkaline solutions containing hydrogen peroxide has an anti-catalytic effect, presumably to be attributed to the colloids resulting from the hydrolysis of the silicates.

It is interesting to note that the combined effect of a mixture of two different stabilizers may exceed the sum of the effects of the two when used separately (24). This result is reminiscent of the reversed state of affairs, reported concerning the effect of a mixture of two catalysts, in which case the rate of decomposition of the hydrogen peroxide was increased by an amount greater than that corresponding to the sum of the two catalytic effects when employed separately.

It is obviously necessary that the pH of the hydrogen peroxide solution should lie within the range over which the two stabilizers are effective when used individually. For example, in 90% hydrogen peroxide, sodium stannate is most effective if the pH of the hydrogen peroxide solution (at ten-fold dilution) falls between 3.5 and 6 (see footnote, page 34). At a pH of 2, or of 7, the decomposition rate for the same solution may rise as much as twenty-fold (23).\*

#### Oxine

Of the stabilizers which have been studied, especially in the case of highly concentrated hydrogen peroxide, particular mention has been made of such organic substances as 8-hydroxyquinaline, ("oxine"), often used as the pyrophosphate derivative or in conjunction with a soluble phosphate or pyrophosphate\*\*; and of

\* Reichert and Hawkinson (23a) recommended addition of a buffer, such as a saturated aliphatic acid of ionization constant  $10^{-4}$  to  $10^{-6}$  (preferably adipic acid), in conjunction with stabilization by stannate and pyrophosphate mixtures. The hydrogen peroxide solution (presumably not over 30% hydrogen peroxide) thereby assumed a pH of 3.5 to 4.0.

\*\* A solution of oxine suitable for use with concentrated hydrogen peroxide solution, may be prepared as follows: 19 g. of pyrophosphoric acid are dissolved in 200 ml. of water and 31 g. of oxine added to the solution, which is then heated on a water bath

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sodium stannate. The mechanism of the stabilization process involving "oxine" is not entirely clear in all of its details; for in the presence of iron contamination, oxine alone has little if any protective action, yet in the presence of phosphate, or preferably pyrophosphate, it makes an effective stabilizer against the influence of small concentrations of certain catalytic contaminants, including iron compounds. It was much used by the Germans in the stabilization of 85% hydrogen peroxide for various military purposes during World War II, but, like other organic additives, gradual oxidation by the hydrogen peroxide is to be expected in the event of long-term storage. This becomes more probable if contamination by ferric iron has taken place in the hydrogen peroxide solution, as the oxidation of oxine by hydrogen peroxide is markedly catalyzed by ferric compounds. However, if the stabilizer also contains pyrophosphate ion (as in the example just given), the ferric ion may become inactivated by interaction with pyrophosphate ion, so that the oxidation of oxine is greatly reduced, to the extent that the stabilizing effect of the mixture may be prolonged for many months of storage, even though some slight contamination by ferric ion had taken place.

#### Pyrophosphate

Sodium pyrophosphate ( $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) alone is capable of holding in check at least as great a concentration of ferric ion as 10 p.p.m.  $\text{Fe}^{+++}$ , but is not sufficiently protective against contamination by even a few p.p.m. of copper compounds. Its protective mechanism appears to consist of reaction with such dissolved catalytic ions as  $\text{Fe}^{++}$  which are either precipitated,

for about 20 min. with vigorous stirring until all of the oxine has dissolved. The brown solution is made up to 1 liter and filtered free of any dark flakes. Of this solution 1 or 2 ml. added per liter of the hydrogen peroxide solution should provide adequate stability to 85 - 90% hydrogen peroxide for most purposes, and provide a decomposition rate at 50°C. not in excess of 0.002% per hour, provided that the hydrogen peroxide in the original solution was sufficiently pure.

Another formulation for stabilization by means oxine is the following: 304 mg oxine, 230 mg  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ , and 202 mg  $\text{H}_3\text{PO}_4$ , per liter of solution.

or, in the presence of an excess of pyrophosphate, converted into relatively stable complexes; in either case the catalytic effect is largely eliminated. It seems improbable that pyrophosphate should directly influence the heterogeneous decomposition process, except insofar as it may inactivate metal ions which otherwise may lead by hydrolysis to the formation of catalytically active, solid products. It is also to be borne in mind that pyrophosphate ion is itself subject to gradual hydrolysis at ordinary temperatures in aqueous solutions:  $P_2O_7^{4-} + H_2O \rightleftharpoons 2HPO_4^{2-}$ . It is, of course, essential that the pyrophosphate employed for stabilization purposes should itself be chemically pure and, in particular, free from iron contamination.

The ratio of pyrophosphate ion to ferric ion found (?) to be required for satisfactory stabilization of iron-contaminated concentrated hydrogen peroxide solutions at 50°C. is shown in Table 2:

TABLE 2  
OPTIMUM PROPORTIONS OF PYROPHOSPHATE  
FOR STABILIZATION AGAINST FERRIC ION (?)

$Fe^{+++}$ (added as sulfate), p.p.m.	Avg. $P_2O_7^{4-}$ required (added as $Na_4P_2O_7 \cdot 10H_2O$ ), p.p.m.	Ratio, $P_2O_7^{4-} : Fe^{+++}$
0.08	0.30	3.8
.16	.60	3.8
.24	1.10	4.6
.32	1.60	5.0
.48	2.50	5.2
.96	7.40	7.7
1.08	10.00	9.3
1.92	17.20	9.0

#### Stannate

Sodium stannate,  $Na_2SnO_3 \cdot 3H_2O$ , as has been previously indicated, forms by its hydrolysis colloidal hydrous stannic oxide,  $SnO_2 \cdot xH_2O$ , which adsorbs catalytic ions, such as ferric ions, in an effective manner and hence improves the stability of hydrogen peroxide solutions. If added in excessive proportions,

the hydrolysis of sodium stannate increases the pH of the hydrogen peroxide to a point which may result in a reduction of its stability. Sodium stannate is not outstanding in its effectiveness against contamination by copper compounds. To adequately restrain the catalytic influence of as little cupric ion as 0.1 p.p.m., it was found necessary to add up to 65 p.p.m. of  $\text{SnO}_2$  (added as stannate). Furthermore, its effectiveness in stabilization has been observed to be somewhat time-dependent, as discussed below. The temperature and temperature history also affects its activity, thus, the stability of stannate-stabilized hydrogen peroxide was observed to be improved by a preheating of the solution to 50°C. before measurements were carried out at 30°C.

If a stabilizer is added in increasing amounts to a given sample of hydrogen peroxide, the rate of decomposition will drop to a minimum, and then slowly increase. Consequently, there exists an optimum amount of stabilizer, which is a function of the kinds and amounts of impurities present. Table 3 shows the proportions of stannate found (7) most effective in controlling the catalytic effect of ferric ion when the latter was present at concentration of from 0.1 to 4.0 p.p.m. in 85% hydrogen peroxide. The rate of decomposition of the original, uncontaminated hydrogen peroxide varied somewhat (from about 0.003 to 0.004% per hr. at 50°C.) as shown in the first column; the stabilized material showed decomposition rates of about 0.0001 to 0.002% per hr., and the optimum amount of  $\text{SnO}_2$  (added as  $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ ) is seen to range from about 1 to 60 p.p.m.; the ratio of  $\text{SnO}_2:\text{Fe}^{+++}$  employed varying from 13 to 26 for iron contents above 0.3 p.p.m.

In place of adding sodium stannate as a stabilizer, it is also possible to attain similar results by preparing hydrous stannic oxide as a gelatinous precipitate (thoroughly washed by repeated decantations) and adding the hydrous gel to the hydrogen peroxide solution; thus bearing out the belief that stabilization here is brought about by the "scavenging" action of colloidal hydrous stannic oxide (25).

TABLE 3  
OPTIMUM PROPORTIONS OF  $\text{SnO}_2 \cdot x\text{H}_2\text{O}$  FOR STABILIZATION  
AGAINST FERRIC ION (?)

Orig. Rate of Decomposition (% per hr. at 50°C.)	$\text{Fe}^{++}$ added as sulfate (p.p.m.)	Optimum $\text{SnO}_2$ (added as Stannate p.p.m.)	Resulting Rate of Dec. (% per hr.; 50°C.)	Ratio $\text{SnO}_2/\text{Fe}^{++}$ employed
0.0029	0.10	0.83	0.0003	8.3
0.0029	.27	1.98	0.007	7.3
0.0034	.29	1.75	0.0013	6.0
0.0020	.31	7.00	0.0007	22.6
0.0037	.35	5.24	2.0013	15.0
0.0031	.47	7.79	0.0015	16.6
0.0046	.55	11.1	0.0006	20.2
0.0029	.85	11.3	0.0013	13.3
0.0040	1.09	17.5	0.0005	16.0
0.0029	1.52	23.3	0.0017	15.3
0.0020	1.80	47.0	0.0020	26.1
0.0023	2.72	63.1	0.0021	23.2
0.0040	3.99	61.5	0.0037	15.4

These results have been confirmed by several independent investigators (25a). Another expedient suggested by Gilbert and Reichert (23b) employs as a stabilizer  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ , heated for one hour at 300°C. with 85% phosphoric acid (to convert the latter to pyrophosphoric acid). For best results, the hydrogen peroxide solution should be kept at a pH below 5.

Measurements of the decomposition rate of concentrated hydrogen peroxide solutions stabilized with sodium stannate have indicated that the stabilizing action requires some time to attain its maximum effect--usually the rate has been observed to decline slowly over a matter of three or four days before leveling off to an essentially constant value.\*

\* In this connection, Giguère and Geoffrion (2), reported a brief delay (30 to 60 min.) in the appearance of a stabilizing effect when a small quantity of sodium stannate was added to dilute hydrogen peroxide solutions. Conceivably this delay resulted from the time required to build up in the solution a sufficient quantity of colloidal stannic oxide, by hydrolysis of the stannate, to bring about the desired stabilization effect.

### Other Stabilizers

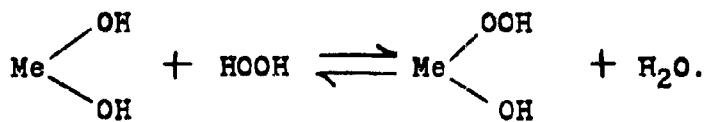
The behavior of hydrous zinc oxide is also of interest. When zinc salts, such as the sulfate, are added in the proper proportion to very concentrated hydrogen peroxide solutions (of the order of 90% hydrogen peroxide) they exert a stabilizing action upon the latter, at least over a limited range of pH (14). In more dilute hydrogen peroxide solutions, however, (say, 20 - 30% hydrogen peroxide) the effect is reversed and the decomposition rate of the hydrogen peroxide is observed to be actually increased somewhat by the addition of soluble zinc salts.

The fact that the presence of zinc oxide in dilute solutions of hydrogen peroxide fails to stabilize the latter, and in fact may even result in an increase in the decomposition rate, has been interpreted by Pierron (26) on the basis of the hypothesis that metal oxides which act as stabilizers are converted into

hydrated peroxides, as  $\text{MeO} \longrightarrow \text{Me} \begin{array}{c} \text{OOH} \\ \diagdown \\ \text{OH} \end{array}$ , or  $\text{MeO}_2 \cdot \text{H}_2\text{O}$ ; or possibly  $\text{MeO}_2 \cdot \text{H}_2\text{O}_2$ , or  $\text{Me} \begin{array}{c} \text{OOH} \\ \diagdown \\ \text{OH} \end{array}$ . According to Pierron, if the proportion

of metal oxide to hydrogen peroxide is such as to lead to incomplete metal peroxide formation, there will be either feeble stabilization or a slight acceleration of the decomposition process. With metal oxides which are pronounced decomposition catalysts (such as oxides of lead, copper, manganese, silver or mercury), the presumption is that peroxide formation is either very small or non-existent, due to the unstable character of such peroxides.

It would appear reasonable to attribute the relationship existing between the concentration of the hydrogen peroxide and the stabilizing action of such a substance as zinc oxide or hydroxide to the possibility of displacement of the equilibrium in such a reaction as:



If, according to Pierron, the peroxidized metal hydroxide is the active stabilizing agent,\* it will be most effective in the presence of excess hydrogen peroxide; and it will be hydrolyzed in dilute hydrogen peroxide solution with reversion to the metal hydroxide (or to the hydrous, or hydrated oxide).

D'Ans and Mattner (27) studied the stabilizing of alkaline solutions of hydrogen peroxide against catalytic decomposition caused by the presence of cupric hydroxide, by addition of magnesium hydroxide. They reported the removal of traces of heavy metals, especially of copper, by means of the precipitated  $Mg(OH)_2$ , thereby effecting a purification of the hydrogen peroxide solution.

From what already has been said concerning the intrinsic stability of pure hydrogen peroxide, it is apparent that, if this substance could be prepared and preserved in the total absence of catalytically active materials, no stabilizers would be needed to insure the possibility of storage for long periods at ordinary temperature without appreciable loss by decomposition. In line with this reasoning, several industrial manufacturers are now producing high concentration, unstabilized hydrogen peroxide which is nearly completely free of additives, and yet may be transported and stored safely in aluminum drums.

The list of the many other substances which have been applied to the stabilization of hydrogen peroxide of various concentrations, including inorganic as well as organic compounds, is lengthy and no attempt will be made to record them all here.\*\*

A representative list of such organic and inorganic stabilizers for dilute hydrogen peroxide solutions was studied by Sonol (28), among others, and the comparative effectiveness of

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\* It is not apparent why the peroxidized hydroxide should be capable of effecting stabilization if the hydroxide or oxide are without similar action.

\*\* The reader is referred to such sources as Machu's "Das Wasserstoffperoxyd und die Peroxverbindungen," second edition, Springer-Verlag, Vienna, 1951, for a detailed list of such stabilizers.

the different substances was reported, when added at concentrations from 0.25 to 0.50%.

Among the various organic substances which have been suggested for the stabilization, especially of dilute hydrogen peroxide solutions, acetanilide has been very commonly employed. However, the shelf life of 3% hydrogen peroxide solutions thus stabilized is considered to be only about 6 months (29); furthermore, acetanilide has been reported more subject to oxidation (to nitrobenzol) than phenacetin (29). Likewise, p-hydroxybenzoic acid ester (so-called "Nipagin-M") has been said to be superior to many other similar preservatives. The presence of benzoic acid (0.1%) was found effective in concentrating hydrogen peroxide solutions by a distillation process (30).

Foligner and Schneider (31) also made a study of the stabilizing effects of addition of small proportions of aliphatic ketones, esters, and alcohol sulfonates, as well as ammonia and some inorganic salts (sodium borate, silicate, phosphate, and pyrophosphate) to "bleach liquor" at 40°, 50° and 70°C. over a period of 96 hours. Their tabulated results show the superior effectiveness of sodium pyrophosphate (particularly at higher temperatures) among the inorganic stabilizers. Some of the organic substances were found to be good wetting agents as well as stabilizers.

Carrara and Monzini (32) observed the stabilizing properties of a series of azoxy compounds of the sulfonamides; Kunz (33) reported the similar effect of addition of antipyrine; and Harris and Fahs (34) that of hydroquinone or its derivatives.

It has been emphasized, however, that many organic additives are subject to a gradual oxidation, which at room temperature may result in the protective action being lost within a period of a few weeks or months of storage of even dilute solutions of hydrogen peroxide.

#### The Choice of a Stabilizer

In comparing the relative merits of the various stabilizers which have been applied to the preservation of dilute

or concentrated solutions of hydrogen peroxide, a natural query may arise as to the possibility of designating one of these agents as the best of all in its effectiveness in this regard. However, it is scarcely possible to give an unqualified reply to such a query, particularly because the selection of a stabilizer must be made with due regard to the conditions under which the hydrogen peroxide ultimately is to be used, as well as to such considerations as the required length of time of storage and the probable prevailing temperatures which the solution will be required to withstand during the storage period. As has been pointed out above, if the storage period is to be relatively brief, an organic stabilizer may be satisfactory, whereas over a prolonged period of time slow oxidation may destroy the effectiveness of an organic component. On the other hand, for certain purposes limitations may be placed upon the choice of an inorganic stabilizer due to the quantity of undesirable residual matter which may be left after a large quantity of the hydrogen peroxide has been decomposed in use.

#### The Mechanism of Stabilization

A completely satisfactory explanation of the various mechanisms whereby stabilization of hydrogen peroxide is brought about, by the wide variety of organic and inorganic substances which have been employed for this purpose, has not been presented up to the present time; although in certain individual cases the evidence is rather conclusive. The effect of addition of small quantities of some acids already referred to, in repressing the dissociation of  $H_2O_2 \rightarrow H^+ + OOH^-$ , appears clear enough, as does the role of various additives which are known to be able to form complexes with certain active catalytic ions which may be present. Again, we have seen that some stabilizers are obviously effective as protective colloids. The increase in the viscosity and the change in the surface tension of hydrogen peroxide solutions in the presence of such colloidal materials as gelatine, starch or glue, may account in part for the restraining action of these additives upon the decomposition of hydrogen peroxide. If the

decomposition process is viewed as dependent upon the formation of activated molecules, induced by the presence of positive catalysts, then it would seem reasonable to assume that stabilizers may function by inactivating or preventing the formation of such activated molecules.

In this connection, Richter (35) studied the effect of various organic substances as inhibitors on the photochemical and the enzymic decomposition of hydrogen peroxide. He observed that the enzymic reaction is comparatively little influenced by the presence of inhibitors, and concluded that the decomposition process in this case does not involve a chain mechanism, such as is suggested in the case of the photochemical decomposition reaction.

In some cases stabilization practices have been found empirically to be useful without the development of an adequate accompanying theoretical interpretation of the phenomenon. One fact appears established, namely, that although stabilizers may restrain the decomposition process, yet the process itself is not thereby fundamentally altered--it retains its monomolecular character in the presence of the inhibiting agent.

#### THE EFFECT OF pH UPON THE DECOMPOSITION RATE OF HYDROGEN PEROXIDE

If the decomposition rate of a given concentration of unstabilized hydrogen peroxide, in aqueous solution and as free as possible from contaminants, is plotted as a function of pH--the latter being controlled by addition of the purest sulfuric acid or of sodium hydroxide solutions--a curve is obtained which shows a minimum at a pH (measured at ten-fold dilution\*) in the

\* By reference to Figure 6 it will be apparent that, if the pH of undiluted hydrogen peroxide solutions having concentrations greater than 90 wt. % is measured with the aid of the glass electrode, negative readings are obtained, which are not open to the usual mode of interpretation. Dilution to one tenth of the original concentration was employed as an expedient, so that the pH data thereby obtained might be compared and interpreted in the usual way.

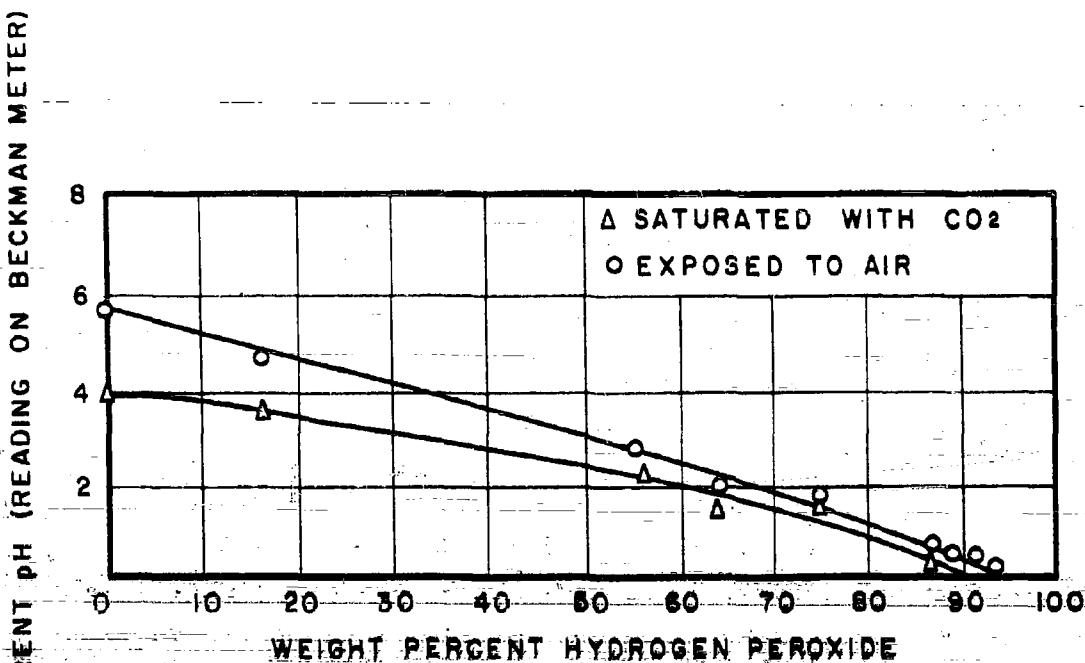


FIG. 6 - MEASURED pH OF HYDROGEN PEROXIDE SOLUTIONS IN CONDUCTIVITY WATER

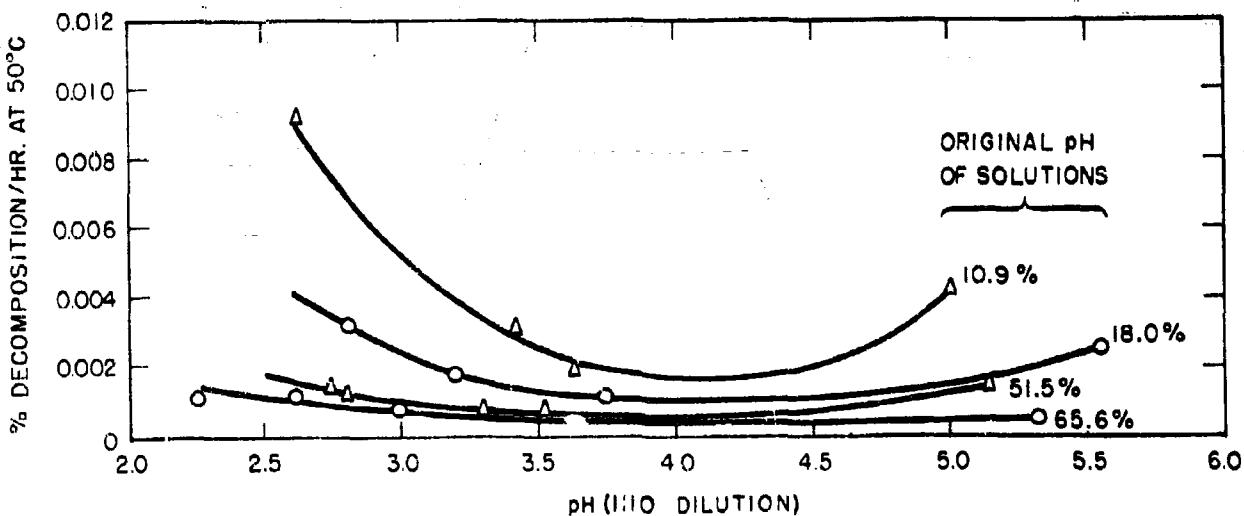


FIGURE 7-RATE OF DECOMPOSITION OF H<sub>2</sub>O<sub>2</sub> OF VARYING CONCENTRATIONS WITH CHANGE IN pH, AT 50°C. (pH ADJUSTED WITH H<sub>2</sub>SO<sub>4</sub>)

vicinity of about 4.5 to 5.0. The decreasing stability in the higher ranges of pH is readily accounted for, as indicated above, on the basis of the equilibrium expression:

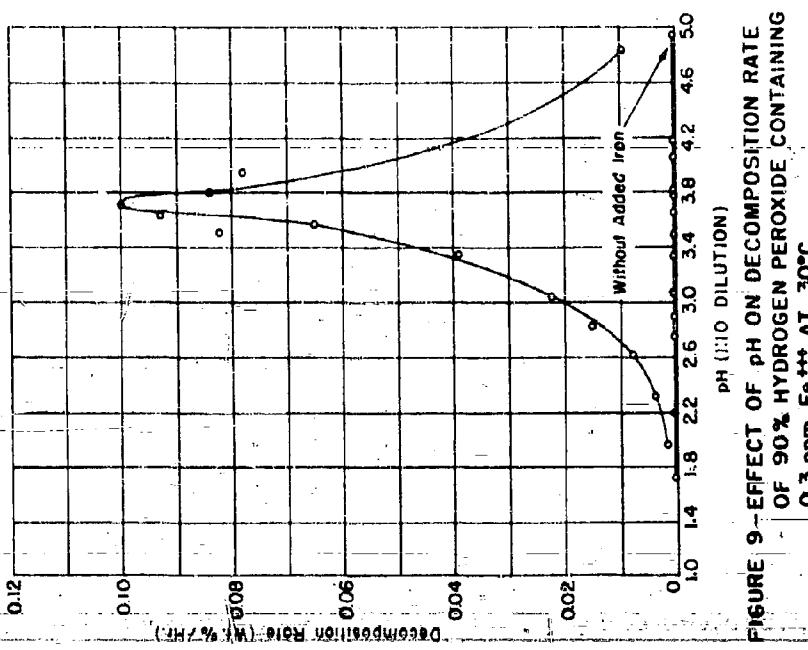
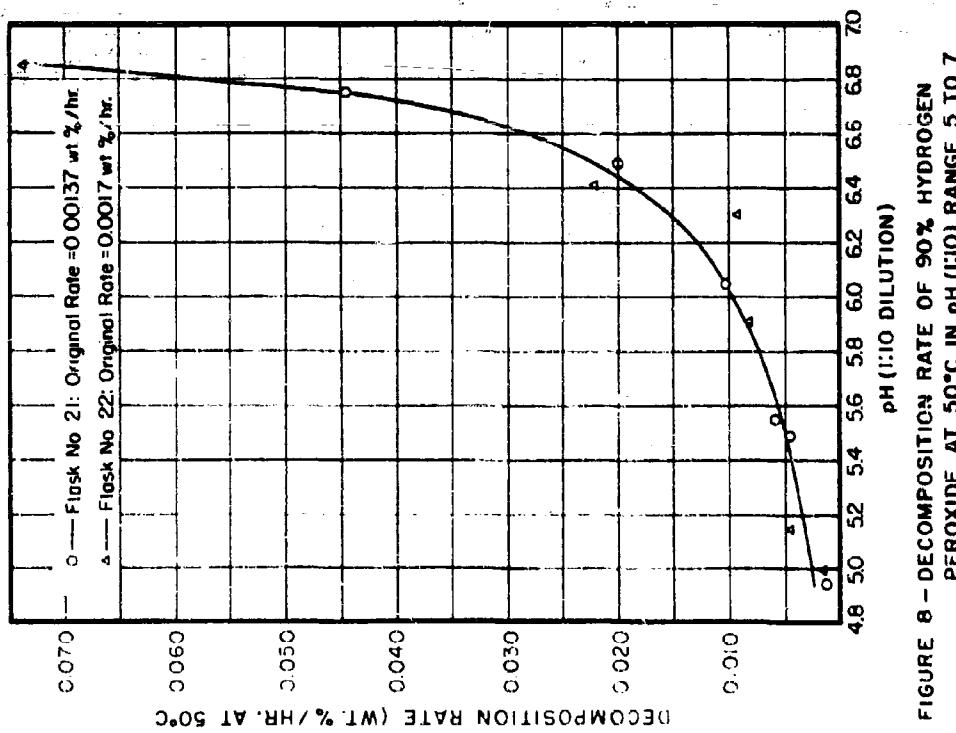
$\text{HOOH} \longrightarrow \text{H}^+ + \text{OOH}^-$ , in which the perhydroxyl ion,  $\text{OOH}^-$ , reputed to be unstable, would be expected to increase in concentration as that of the hydrogen ion is diminished by addition of alkali.

The sharp decrease in stability at the other extreme of the pH scale, at  $\text{pH}_{(1:10)}$  values of about 1 to 2, is less easily accounted for, however. In lower concentrations of hydrogen peroxide, say 30 wt. % or less, the increase in the decomposition rate at low pH is more noticeable than in the case of more concentrated solutions. In somewhat more concentrated solutions, over the range of  $\text{pH}_{(1:10)} = 2$  to 6, only a small effect of pH change is noted.

For concentrations of  $\text{H}_2\text{O}_2$  above 50% by weight the effect of variation in pH, over the range 2.5 to 5.5, upon the rate of decomposition of hydrogen peroxide is but slight; at concentrations progressively lower than 50%, the effect of variation in pH becomes increasingly important, both in the lower and high ranges of pH.

Figure 7 shows the results of measurements in which the decomposition rates of dilute and more concentrated solutions of hydrogen peroxide were measured over a wide range of pH. It will be observed that the general form of the individual curves is similar, with maximum stability (or minimum decomposition rate) falling in approximately the same pH range,  $4.0 \pm 0.5$ , in all cases. At a fixed pH it is also to be noted that the more concentrated solutions appear to be more stable than the more dilute solutions, the difference being larger the farther one proceeds in either direction from the region of maximum stability ( $\text{pH}_{(1:10)} = 4.0$ ).

Figure 8 shows the influence of increasing pH over the range  $\text{pH}_{(1:10)} = 5$  to 7 for 90% hydrogen peroxide. The decomposition rate at  $50^\circ\text{C}$ . is seen to rise in a steadily increasing manner as the solution becomes more alkaline.



If, in addition to the effect of changing pH, the catalytic effect of added metal ions, such as  $\text{Fe}^{+++}$ ,  $\text{Cu}^{++}$ , or  $\text{Cr}^{+++}$ , is also introduced, the plot of decomposition rate vs. pH of a 90% hydrogen peroxide solution, for any particular constant quantity of added catalytic ion, may show a remarkable cusp or "peak" in the neighborhood of  $\text{pH}_{(1:10)} 3.5$ , which is not found with hydrogen peroxide solution alone. For the additions of other metal cations, such as  $\text{Ag}^+$ , the maximum may lie at higher pH's. This "peak," with its maximum showing an increase often of ten-fold or more over the corresponding value obtained in the absence of the catalyst, may occur over a remarkably small interval of pH (as small as about one pH unit); so much so, that if only a few points are taken to establish the shape of the curve, the peak may be entirely missed. The peak, furthermore, is not observed in the case of such added ions as  $\text{Al}^{+++}$ , which the possibility of a rise to a higher oxidation state is not afforded, and consequently a catalytic cyclic mechanism, involving an alternation between two oxidation states, is excluded.

From the general shape of the decomposition rate-pH curve shown in Figure 9, it is apparent that the peak in the upper curve represents the resultant effect of conditions superimposed upon those leading to the lower curve. Instead of resulting in a similar curve, raised above the values at corresponding pH's in the lower curve, it is found that, on the addition of a suitable contaminant, a branch appears representing a sharp acceleration in the decomposition rate with increasing pH, followed by a branch in which a rapid drop in the rate occurs as the pH is further increased.

A reasonable interpretation of this behavior has been suggested (7, 36), in which the sharp increase in decomposition rate was attributed to the progressive hydrolysis of the dissolved catalyst (e.g., a ferric salt) forming a colloidal hydrous oxide (or possibly slightly soluble basic salts), with a relatively large catalytically active surface in contact with the

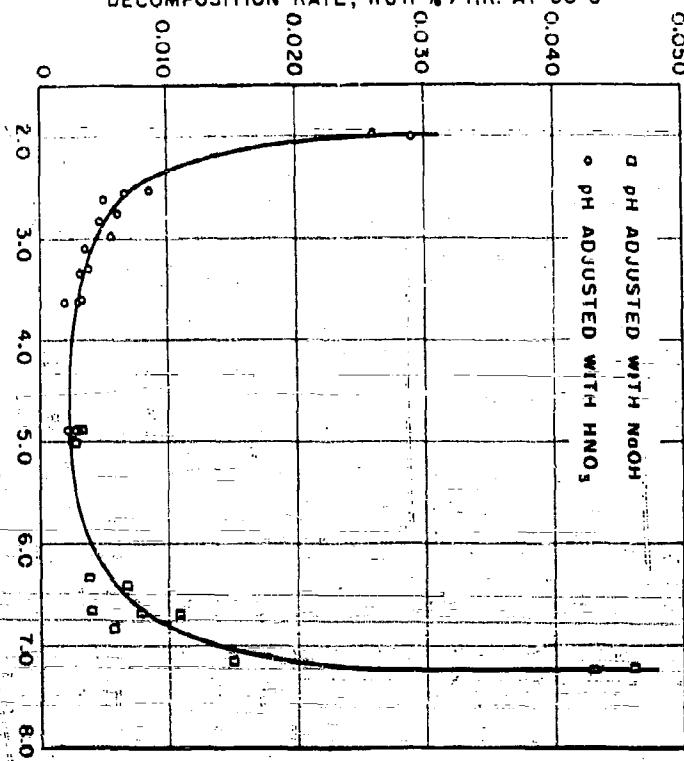
hydrogen peroxide solution. This would cause the heterogeneous decomposition reaction to accelerate with rising pH. The rapid decline in decomposition rate at higher pH values was interpreted to mean that coagulation of the colloid was occurring, with a resultant sharp decline in the surface area of the hydrous oxide exposed to the solution. At still higher pH values (not shown in the figure) another rise in the decomposition curve is to be expected, due to the increasing alkalinity of the solution, as was seen in Figure 8. The minimum preceding this rise would lie higher than that expected in the low pH range, as the coagulated colloid presents some catalytically active surface, although much less in extent than that offered by the dispersed phase.

Another interesting example of the catalytic effect of certain added contaminants is shown in Figure 10, in which the influence of 0.2 p.p.m. of lead ion, added in the form of lead nitrate, is observed over a range of pH<sub>(1:10)</sub> of 2 to about 7.2. The pH adjustment was made by addition of either nitric acid or of sodium hydroxide. In keeping with the fact that the pH at which precipitation of lead hydroxide begins to occur is about 6, as compared to a pH of about 2 for hydrous ferric oxide, we do not expect a sharp cusp in the decomposition rate curve in the vicinity of 3.5. (This was looked for carefully, as the experimental points indicate.) The "peak," if any occurs, would be expected in the high pH range, at which decomposition is progressing rapidly even in the absence of other added catalytic substances.

The influence of increasing quantities of a given catalytic contaminant, such as ferric ion, over a limited range of pH, is indicated in Figure 11, in which the concentration of ferric ion is increased stepwise from 0.1 to 1.0 p.p.m., while the pH<sub>(1:10)</sub> range is from 1.6 to 3.2.

Even in the case of contamination by compounds of such elements as manganese and silver, the importance of the pH factor is very significant: in sufficiently acid solutions of concentrated hydrogen peroxide neither silver nor manganous ions exert

DECOMPOSITION RATE, WGT. % / HR. AT 50°C

FIGURE 10 - EFFECT OF pH ON DECOMPOSITION RATE OF 90% HYDROGEN PEROXIDE CONTAINING 0.2 ppm  $Pb^{2+}$  (ADDED AS  $Pb(NO_3)_2$ ) AT 50°C

DECOMPOSITION RATE, WEIGHT % PER HOUR AT 50°C

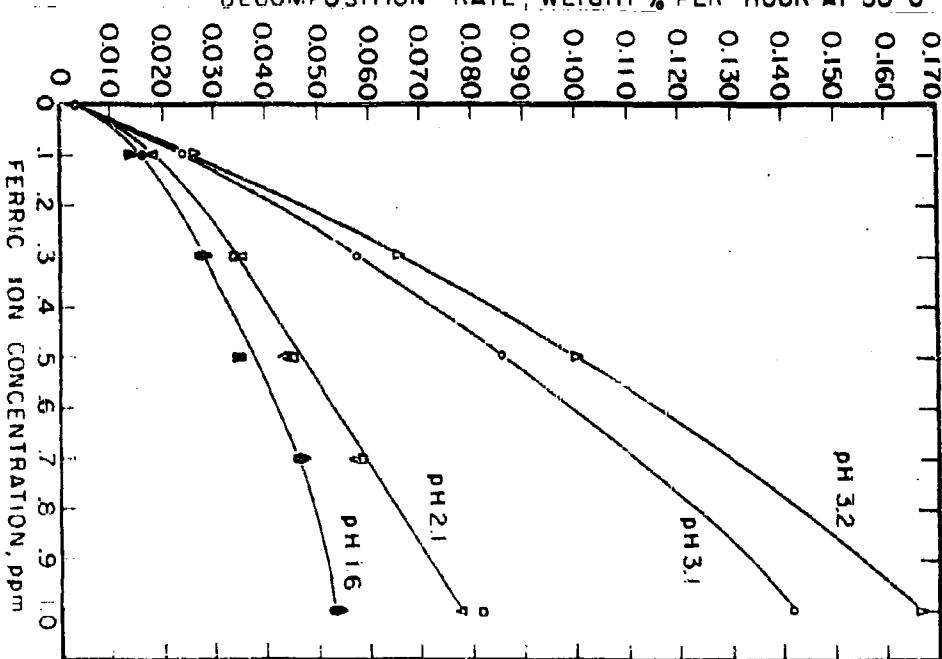


FIGURE 11 - EFFECT OF pH (1:10 DILUTION) AND FERRIC ION CONCENTRATION ON THE DECOMPOSITION RATE OF 90% HYDROGEN PEROXIDE AT 50°C

any pronounced catalytic activity. They are presumably present in solution as the simple cations. When, however, the pH is caused to increase sufficiently so that the oxides of these metals may precipitate, a rapid and great increase in the decomposition rate of the peroxide ensues.

It is evident, in view of these considerations, that in order to properly compare the stabilities of different samples of hydrogen peroxide the prevailing pH of the solution must be specified; and this requirement is the more important if known contamination by catalytic substances exists in the solution.

It is also evident, from what has been presented previously, that for the long-term storage of hydrogen peroxide solutions, the materials of construction of the container must be scrupulously clean and must be devoid of catalytically active components. Considerable attention has been given to this subject, and a number of articles have appeared in which comparative measurements of stability of hydrogen peroxide solutions in containers of different composition are recorded. Further details will be found in Chapter 4.

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## CHAPTER TEN

### ANALYTICAL PROCEDURES

Two aspects of the analysis of solutions containing hydrogen peroxide are clearly differentiated: it is of importance to be able to detect or to determine the hydrogen peroxide content of such solutions, whether present in minute proportions or as the major component of the mixture; and also to establish the presence of impurities or additives in dilute or concentrated hydrogen peroxide solutions, especially such substances as are known to affect the stability of the solution. The first of these requirements is met by the application of various standard qualitative or quantitative methods of analysis for any except the most minute concentrations of hydrogen peroxide; and even for such very dilute solutions certain sensitive color reactions, described below, are available for the detection, and in some cases for the estimation, of the quantity of hydrogen peroxide present. In the following sections the qualitative and quantitative procedures which have been developed for the analysis of hydrogen peroxide solutions are described.\*

#### QUALITATIVE ANALYSIS

Of the various reactions which may be employed for the detection of hydrogen peroxide, or of a peroxy compound which may yield hydrogen peroxide, a number of color tests have been suggested, some of which are of high sensitivity. For example, the orange color which is developed by titanic acid in the presence of hydrogen peroxide is characteristic and delicate (1).

Titanium sulfate solutions, prepared from commercial titanium sulfate (empirically written as  $\text{TiOSO}_4$ , containing about

\* An early comprehensive account of the analytical aspects of hydrogen peroxide may be found in "Untersuchungsmethoden des Wasserstoffperoxyds," by L. Birckenbach, in "Die Chemische Analyse," Vol. VII, B. M. Margaschka, Ed., Stuttgart, F. Enke, 1909.

20%  $TiO_2$ ) by shaking with an equal weight of water and filtering,\* is perhaps the most commonly used reagent for this purpose and as little as 1 or 2 p.p.m. of hydrogen peroxide can be detected by the yellow color produced by an acidified hydrogen peroxide solution. The color has been ascribed to the formation of such an ion as  $[TiO_2(SO_4)_2]^-$  (2). This reaction has been employed also as the basis of a quantitative procedure, with the aid of a photoelectric colorimeter. One microchemical form of this test for hydrogen peroxide described by Berisso and Aquisso (3) employs a 10%  $Ti(SO_4)_2$  solution in 6 N  $H_2SO_4$  and pure amyl alcohol. On shaking 3 ml of each of the two liquids together and allowing the two layers to separate, 1 ml of the alcoholic layer is transferred to another tube and a drop of the hydrogen peroxide solution added. The yellow color of peroxytitanic acid is very sensitive and specific. Very few other oxidants in acid solution show a similar reaction toward titanium solution. Thus, the yellow color with  $Ti(SO_4)_2$  is not produced by ozone (4) nor with peroxy sulfates (5). The quantitative application of this test is described below. The yellow color does not fade out quickly, in contrast with certain other colored compounds of lower stability, such as the blue peroxychromic acid, which has been much used for the same purpose. In this latter test, a few drops of a dilute solution of potassium bichromate are added to a test tube containing about a milliliter of the solution to be tested (acidified with a few drops of dilute sulfuric acid) and several milliliters of ether. On shaking, a blue color developing in the ether layer, attributed to peroxychromic acid,  $HCrO_5$ , indicates the presence of hydrogen peroxide in the test solution. There is disagreement as to whether or not the test is given by ozone; but in the absence of the latter it may be relied upon for the detection of about 0.2 mg of hydrogen peroxide in the concentration of about 0.001%.

\* Alternatively, commercial  $TiO_2$  may be fused with 15 - 20 parts of  $K_2S_2O_7$  and, after cooling, the fusion may be dissolved in cold, dilute sulfuric acid.

Another sensitive color reaction is the so-called Schern-Schellhase reaction (6), in which a blue color results from the interaction of a freshly prepared, alcoholic, dilute solution of guaiacum resin, containing diastase, with hydrogen peroxide, which is said to be detected in dilutions up to 50 million parts of water. This reaction has been applied, e.g., to the detection of hydrogen peroxide in milk (7). Other oxidizers, however, such as ozone, chlorine, or nitrous acid, also give the color with guaiacum tincture, even without addition of diastase.

One of the very sensitive qualitative tests for hydrogen peroxide is the decolorizing of black lead sulfide, forming white lead sulfate. Application has been made of this reaction in a microchemical test, in which lead sulfide is formed on photographic paper, which, after fixing, is treated with dilute lead acetate solution followed by a solution of hydrogen sulfide. Application of a solution containing less than 0.001 mg hydrogen peroxide to the printing paper results in a lightening of the color of the lead sulfide (8). Further refinements of this test (9) are reported capable of detecting  $0.01 \gamma$  ( $1 \times 10^{-5}$  mg) hydrogen peroxide in a limiting concentration of 1 in  $5 \times 10^7$  p.b.w. of solution. The test will also be given by other oxidizing agents.

The reducing as well as the oxidizing characteristics of hydrogen peroxide have been drawn upon for the detection of this substance. Thus, Feigl and Frankel (10) describe several spot tests for hydrogen peroxide, including its reducing action upon a dilute mixture of ferric chloride and potassium ferri-cyanide, resulting in the formation of Prussian blue. As little as 0.0001 mg of hydrogen peroxide can be detected in this way in a concentration not much above 1 part per million. Reduction of solutions of gold salts, yielding blue or red colloidal solutions of gold, is employed in another test of approximately equal sensitivity. Similarly, hydrogen peroxide reduces nickel(III) oxide with a consequent lightening of the color, and a microchemical test, depending upon this effect, is said to be capable of detecting as little as  $10^{-5}$  mg of hydrogen peroxide in a concentration of 0.2 p.p.m.

Certain of the colorimetric methods which have been adapted to the quantitative determination of hydrogen peroxide are mentioned below. Another interesting qualitative test for hydrogen peroxide depending upon the luminescence produced in the presence of luminol reagent (3-amino phthalic hydrazide) catalyzed by hemin was first observed by Gleu and Pfannsteil (11) and was discussed by Langenbeck and Ruge (12), and also by Steigmann (13). The reagents employed by Steigmann consisted of solutions of luminol and of cupric sulfate and a fresh solution of sodium peroxydisulfate,  $\text{Na}_2\text{S}_2\text{O}_8$ . A mixture of the three solutions in appropriate quantities shows luminescence with as little as  $0.2 \gamma (2 \times 10^{-4} \text{ mg})$  of hydrogen peroxide. The test, however, is not completely specific, as other substances, such as peroxybenzoic acid and ammonium peroxydisulfate, are able to produce chemiluminescence also, though at not very high dilutions (about 0.01%). Other aspects of sensitive methods of detection of hydrogen peroxide based upon luminescence phenomena were discussed by Schales (14).

A sensitive color test for hydrogen peroxide which can detect 0.2 mg of hydrogen peroxide per liter and described by G. Deniges (15) depends upon the facts that in ammoniacal solution ferricyanide is reduced to ferrocyanide with liberation of oxygen and that orange  $\text{Ag}_3\text{Fe}(\text{CN})_6$  is readily soluble in dilute ammoniacal solution, whereas white  $\text{Ag}_4\text{Fe}(\text{CN})_6$  is insoluble. A reagent containing silver ferricyanide dissolved in ammoniacal solution reacts with a solution containing hydrogen peroxide forming a white turbidity. Silver ferrocyanide crystals present a characteristic cruciform appearance. If the peroxide concentration is very small, 5 to 10 min standing may be required for the turbidity to appear. Somewhat similarly, the reduction of the ferricyanides of copper or zinc was suggested by Kohn (16) as sensitive reactions for the detection of hydrogen peroxide by means of a color change.

The familiar color test for hydrogen peroxide depending upon the formation of blue, ether-soluble peroxychromic acid has been made still more sensitive by the use of diphenylcarbazide

which reacts with the peroxychromic acid to produce a reddish violet color in the ether layer, whereas the blue peroxychromic acid may be hardly visible. As little as  $5 \times 10^{-6}$  g of hydrogen peroxide in 5 to 10 cc of liquid may be detected in this way (17).

A highly sensitive spot test for hydrogen peroxide, in which o-tolidine in the presence of  $\text{Fe}^{++}$  gives a blue color with as little as 0.025  $\delta$  of hydrogen peroxide in a dilution of 1:24,000, was reported by L. Kul'berg and L. Matveev (18).

Another sensitive spot test for hydrogen peroxide (19) employs cerous sulfate solution, which is converted by an excess of potassium carbonate solution into a somewhat soluble double salt, with the intermediate precipitation of cerous carbonate. A drop or two of this colorless solution treated on a spot plate with a solution containing hydrogen peroxide develops a yellow or brownish red color as the cerium is oxidized.

A color reaction said to be capable of detecting  $10^{-5}\%$  of free hydrogen peroxide in ether is described by Stamm (20). It consists of the reducing of an alkaline solution containing phenolphthalein by means of zinc dust, and addition of a drop of the diluted, decolorized solution and a drop of a dilute cupric sulfate solution to about 1 ml of the ether sample. A pink color developing at the contact zone shows the presence of free hydrogen peroxide. A similar reaction, somewhat slower, is shown by some organic peroxy compounds, as bis(hydroxyethyl) peroxide. Lecoq (21) has also studied the application of phenolphthalein to the detection of hydrogen peroxide.

Other substances which have been applied to the detection of hydrogen peroxide are tetramethyl-p-phenylenediamine (22), benzidine dihydrochloride (23), 2,7-diaminofluorene (23) and vanillin (24).

The necessity for distinguishing between hydrogen peroxide and various other oxidizing substances has resulted in the development of a number of spot tests for gas phase reactions which, when applied in a comparative manner, make possible the distinction

of hydrogen peroxide from fluorine, oxygen fluoride, ozone or certain combinations of these substances. Davis, et al. (25) employed six spot tests as indicated in Table 1, in which "NR" indicates no reaction.

Mellor (26) cited a number of distinguishing tests for hydrogen peroxide, ozone, chlorine and nitrogen dioxide which are outlined in Table 2. In addition to the reagents shown in Tables 1 and 2 mention may be made of the following procedures. Kaiser and McMaster (27) reported that if a mixture of ozone, hydrogen peroxide, chlorine and nitrous oxide is passed through a solution of potassium permanganate, ozone alone escapes unchanged, and can be shown to react with starch-potassium iodide reagent in the usual way.

Similarly, if a mixture of ozone and hydrogen peroxide is passed through concentrated chromic acid solution, the hydrogen peroxide is decomposed, but the ozone is not affected (28).

In this connection, although ozone and water have been described by some authors as forming hydrogen peroxide and by others as being without interaction (Ref. 26, p. 903), enough doubt remains so that a proposed distinctive test for hydrogen peroxide which is not believed to be shown by ozone must be used with caution.

The related problem of establishing by suitable tests the presence of the peroxide structure, both in the case of inorganic peroxy compounds and more particularly in the extensive field of organic peroxides and other peroxy compounds, has not been solved to date in a completely satisfactory and unequivocal manner.

In this connection, a distinction in the behavior of hydrogen peroxide and organic hydroperoxides, pointed out by Cadle and Huff (29), is to be found in the relative ease with which they interact with a solution of potassium iodide in the pH range of 4 to 7. The times required for a known quantity of the different peroxides to react with a known amount of potassium iodide at 30°C were measured by these authors; who found that,

TABLE 1

 SPOT TESTS FOR DETECTION OF VOLATILE  
 OXIDIZING SUBSTANCES  
 FROM DAVIS et al. (25)

Reagent	$F_2$	$F_2O$	$O_3$	$H_2O_2$	HF
Tetrabase paper	green-blue	violet	violet	NR	NR
Benzidine	green-blue	yellow-brown	yellow-brown	NR	NR
KBr-fluorescein	red	red	NR	NR	NR
Activated Ag.	black, yellow	NR	black	NR	NR
KI-starch	purple	purple	purple	purple	NR
Acid-base	red then bleached	NR	NR	NR	red
	$HF + O_3$	$F_2O + O_3$	$F_2O + HF$	$F_2O + O_2 + HF$	$O_3 + F_2$
Tetrabase paper	violet	violet	violet	violet	violet
Benzidine	blue-green brown	dirty green-brown	yellow-brown	dirty green-brown	blue-green black
KBr-fluorescein	yellow	red	yellow	sl.red	red
Activated Ag.	NR	NR	NR	black	light brown

for example, 90% of the peroxide had interacted in 25 minutes in the case of  $H_2O_2$ ; while 100 minutes and 130 minutes were required for  $CH_3COOH$  and  $C_2H_5OOH$ , respectively.

The differential determination of hydrogen peroxide in mixtures of peroxymono- and peroxydisulfuric acid has received considerable attention (5, 30, 31, 32, 33, 34 and 35). Analysis

TABLE 2  
DISTINGUISHING TESTS FOR HYDROGEN PEROXIDE  
FROM MELLOR (26)

Reagent	Hydrogen Peroxide	Ozone	Chlorine	Nitrogen Dioxide
KI and starch	blue	blue	blue	blue
Indigo solution	bleached	bleached	bleached	bleached
Litmus solution	bleached	bleached	bleached	bleached
Clean silver foil	nil	blackened	white film	unchanged
Mercury bead	nil	tail on glass	white	unchanged
CrO <sub>3</sub> and ether	blue	nil**	nil	nil
Titanic acid	yellow	nil	nil	nil
Tetramethyl base*	nil	violet	blue	yellow to brown
KMnO <sub>4</sub> solution	decolorized	unchanged	decolorized	decolorized

for hydrogen peroxide in the presence of aliphatic peroxy acids was studied by Greenspan and McKellar (36). A procedure for the titration of hydrogen peroxide in the presence of oxalate was recommended by Simon and Reetz (37). Quantitative analysis of hydrogen peroxide in the presence of aldehydes and methanol was studied by Wilson and LeClair (38).

#### QUANTITATIVE ANALYSIS

The most commonly employed quantitative procedures for the determination of hydrogen peroxide include: (1) combined gravimetric and volumetric analysis, consisting of titration with permanganate, ceric, or iodide ions of a weighed sample of the

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\* Tetramethyl di-para-diamidodiphenyl methane. Test papers are soaked in an alcoholic solution of this reagent and are used moist.

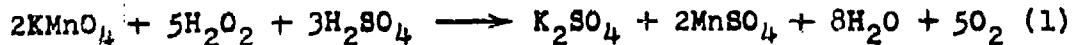
\*\* Other sources report that ozone gives a blue color in this test.

solution; (2) volumetric analysis, consisting, for example, of titration with solutions of permanganate, ceric, or iodide ions of a known volume of the sample, with reference to a density chart; (3) gasometric analysis, measurement of the quantity of oxygen evolved in the catalytic decomposition of a known quantity of the peroxide solution; and (4) physical procedures, such as direct measurement of the density or refractive index of the solution in the absence of other dissolved materials. In addition to these principal methods of analysis, which will be described in some detail, various other procedures have been suggested, which will be briefly referred to below, including colorimetric analysis and catalytic decomposition processes. Conversely, it has been proposed that the determination of the water content of aqueous solutions of hydrogen peroxide may be carried out by titration with the aid of the Karl Fischer reagent (composed of iodine, sulfur dioxide, pyridine and methanol), the end-point being indicated by a brown color due to an excess of iodine (39).

#### Volumetric Methods

Permanganate Titration. This method is one of the most exact and reliable of all the procedures commonly employed in the analysis of hydrogen peroxide. It is applicable both in dilute and in more concentrated solutions with a limit of sensitivity of about 0.1 mg per liter. Organic or inorganic reducing substances which are capable of reacting with permanganate naturally interfere with the method.

The reaction employed was first observed by Brodie (40) and by Schönbein (41), and confirmed experimentally by the work of Aschoff (42) as following the requirements of the equation:



A number of investigators have concerned themselves with establishing the source of the oxygen liberated in this reaction, whether it is formed by contributions from both the hydrogen peroxide and the permanganate, or whether the hydrogen peroxide

alone yields the gas. Although evidence has been presented on both sides of this question, it appears to be clearly established that the hydrogen peroxide alone is the source of the liberated oxygen, and that the oxygen originally constituting part of the permanganate ion appears in the products as water.

The standardization of the potassium permanganate solution used for this analysis is best carried out with sodium oxalate, according to the carefully evaluated procedure of Fowler and Bright (43).

Procedure. Transfer 0.3 g of sodium oxalate (dried at 105°C) to a 600 ml beaker. Add 250 ml of diluted sulfuric acid (5+95) previously boiled for 10 to 15 minutes and then cooled to 27 + 3°C. Stir until the oxalate has dissolved. Add 39 to 40 ml of 0.1 N  $\text{KMnO}_4$  at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds).\* Heat to 55 to 60°C, and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise with particular care to allow each drop to become decolorized before the next is introduced.

"Determine the excess of permanganate required to impart a pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the boiled and cooled diluted sulfuric acid at 55 to 60°C. This correction usually amounts to 0.03 to 0.05 ml."

"In potentiometric titrations the correction is negligible if the end point is approached slowly."

The concentration of the permanganate titration solution is conveniently selected to suit the strength of the hydrogen peroxide solution being tested. A 0.1 N solution is serviceable over a wide range of peroxide concentration other than the most dilute solutions; but concentrations as high as 0.5 N are often employed, with a corresponding increase in the sample weight taken for analysis. As is apparent from inspection of the equation for the reaction, acid is required, which is usually supplied by the addition of dilute sulfuric acid to the solution to be titrated. Hydrochloric acid or other sources of chloride

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\* If the pink color should persist because the permanganate is too strong, discard, and begin again, adding a few ml less of the  $\text{KMnO}_4$  solution.

ion are to be avoided, as the permanganate will also oxidize chloride ion to chlorine, and the titration accordingly will be subject to error. If the presence of chloride cannot be avoided, and particularly if ferric ion may also be present, it is recommended that a manganous salt, such as the sulfate, be added, in the presence of which the oxidation of chloride by permanganate is greatly retarded. The presence of merely a trace of manganous ion in the titration solution furthermore exerts a catalytic influence upon the oxidation-reduction process and ensures instant reaction between the permanganate and the reducing solution. In the total absence of manganous salt the pink color caused by addition of the first few drops of permanganate solution, added in the titration, may require some time to fade out by interaction of the permanganate with the solution being titrated; but as soon as a minimal quantity of  $Mn^{++}$  has been formed the reaction speeds up and the pink color is discharged instantly on mixing with the solution.

The presence in the peroxide solution of organic preservatives, such as salicylic acid, glycerine, etc., obviously may lead to erroneous results by reacting themselves with the permanganate; and large proportions of calcium salts or of titanic acid have been found to lead to low results.

For the analysis of a concentrated solution of hydrogen peroxide, e.g., 90%  $H_2O_2$ , proceed as follows.

Procedure. Into a weighed clean, dry weighing bottle place 10 drops (or not more than 0.75 g) of the 90% hydrogen peroxide solution and reweigh to determine the sample weight.\* Introduce the contents of the weighing bottle, with the aid of a funnel and wash-bottle, into a 500-ml volumetric flask, and when the flask is nearly filled, gently mix the sample by rotating the flask and finally fill to the mark and mix thoroughly by shaking.

To 25 ml of the solution, pipetted from the flask into a 250-ml Erlenmeyer flask, add 1 ml of concentrated sul-

\* In working with dilute solutions, of the order of a few percent of hydrogen peroxide, larger samples, such as 10 g, should be taken.

furic acid. From a burette add 0.1 N  $\text{KMnO}_4$  solution,\* at a rate not over 0.5 ml per second, with constant stirring. The end point is considered as reached when a faint pink color, persisting for 1 minute, is attained. A brown color, due to manganese dioxide, may occur if the permanganate is added too rapidly, or with insufficient stirring, or in the presence of a deficient amount of acid. In any event, such a sample should be discarded, as the results will be in error. The weight percent of hydrogen peroxide is calculated from the results obtained by this procedure, in which an aliquot of 1/20 is taken, by the expression:

$$\begin{aligned} \text{Weight percent } \text{H}_2\text{O}_2 &= (\text{ml } \text{KMnO}_4)(\text{Normality } \text{KMnO}_4) \times \\ &(34.0)/(\text{weight } \text{H}_2\text{O}_2 \text{ sample in grams}) \end{aligned}$$

For routine and somewhat less accurate work the sample may be taken by pipette, and the weight of sample determined by reference to a density chart.\*\* If the degree of accuracy sought requires it, due regard to the change in density with change of temperature must be exercised.

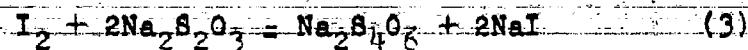
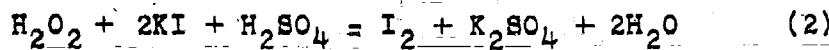
Variants of the above procedure in which permanganate is used include the reaction of the peroxide solution with known quantities of ferrous salts or of stannous chloride, titrating the excess of these reducing substances with permanganate solution. Or, the permanganate may serve to liberate gaseous oxygen, the quantity of which is determined gasometrically. However, in the absence of interfering substances the direct titration, referred to above, appears to be entirely satisfactory. The indirect methods appear to add little to the efficacy of the determination. The accuracy of the permanganate titration for the estimation of hydrogen peroxide was examined by Huckaba and

\* A 1.0 N solution of  $\text{KMnO}_4$  contains 1/5 of a gram molecular weight per liter, so that a 0.1 N solution contains 3.1606 g/l of  $\text{KMnO}_4$ . Thus, 1 ml of 0.1 N potassium permanganate corresponds to 1.701 milligrams of hydrogen peroxide. Such solutions keep well for long periods of time if, when made up, the solution is heated and subsequently filtered through a sintered glass filter before standardization. The bottle should be kept in the dark or protected with a black cloth or other light-proof covering.

\*\* For this purpose it is convenient to prepare a chart of normality as a function of weight percent hydrogen peroxide, using the relation  $\rho \% = 1.7N$ .

Keyes (44) by comparison of the results with those obtained by a catalytic gasometric decomposition method, and good agreement, within 1 part in 5000, between the two methods was reported.

Iodimetric Methods. Somewhat less accurate than the permanganate method yet widely used, especially if the hydrogen peroxide solution is not too dilute (1 to 6%), is Kingzett's method (45), in which slightly acidified potassium iodide solution is employed, (preferably in the presence of a trace of ammonium molybdate as a catalyst (46)). The reactions involved are the following, in which it is to be noted that the iodide ion acts as a reducing agent:



A typical procedure consists of the addition of the peroxide solution, appropriately dilute, to 50 cc of a 1% KI solution, acidified with 1 cc of 1:4  $\text{H}_2\text{SO}_4$  solution, and warmed to 40°C. After stirring and allowing to stand for 5 minutes, the iodine liberated is titrated with thiosulfate solution, with or without the use of starch indicator. Since on prolonged standing of an acidified potassium iodide solution in contact with air liberation of iodine may be expected without further added reagents, it is desirable to correct the results of this iodometric process by means of a blank run with a similarly acidified potassium iodide solution left to stand under the same conditions of time and temperature.

It is obvious that this method cannot be used in the presence of other oxidizing agents which are capable of liberating iodine from an iodide, such as chlorine, ozone, nitric oxide or nitrous acid; or of unsaturated organic substances which could react with the liberated iodine.

Other Volumetric Methods. Ceric sulfate titration has also been recommended. (47) for the determination of the concentration of hydrogen peroxide solutions, especially in the presence of

organic matter. It is reported that in the presence of peroxide-free ether, ethanol, or a mixture of the two, the ceric ion titration to the ferrous-1,10-phenanthroline end point, or to an electrometric end point, gives more satisfactory results than the permanganate titration. Ceric sulfate solution can be employed in a manner exactly analogous to the titration with permanganate, but the end point is somewhat less distinct (19). Rhodamine 6G is recommended (48) as an indicator for the titration with ceric ion.

A volumetric procedure for the determination of hydrogen peroxide which depends upon its reducing properties employs an excess of potassium iodate solution, in the presence of considerable hydrochloric acid. The iodine liberated is oxidized to iodine monochloride in the presence of an indicator\* and in the presence of a trace of excess iodate the indicator is decolorized. The method is not specific for hydrogen peroxide, having been employed with various other reducing agents, such as ferrous and thallous ions, thiocyanate, thiosulfate, and bisulfite ions, hydrazine and phenylhydrazine, etc. (49).

Other methods include potentiometric titration with alkaline sodium chlorite solution (30), which is said to be applicable in the presence of such peroxy salts as  $K_2S_2O_8$ ,  $K_2SO_5$  or peroxyphosphates. Titration potentiometrically with  $K_3Fe(CN)_6$  in the presence of potassium hydroxide was also described by these authors, while Singh and Malik (50) employed  $Na_2SO_3$  as reducing agent in acid solution with excess potassium iodide in a potentiometric process.

Deniges (51) also developed a volumetric ferricyanide method. Belcher and West (52) applied mercurous nitrate as a reductometric agent for hydrogen peroxide determination.

Schwicker (53) used an excess of  $KHSO_3$  to reduce hy-

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\* The dyestuffs Amaranth, Brilliant Ponceau SR, and Naphthol Blue Black (British Color Index Nos. 184, 185, 246, respectively) may be used as indicators. They are not destroyed by high concentrations of hydrochloric acid.

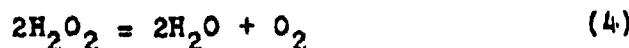
drogen peroxide, the resulting free sulfuric acid being determined by titration with sodium hydroxide after addition of sufficient 3% formaldehyde solution to react with the excess of bisulfite. Van der Meulen (32) titrated hydrogen peroxide in the presence of peroxyulfate by osmic acid; followed thereafter by determination of the peroxyulfate by the ferrous ion-permanganate method. Potentiometric determination of hydrogen peroxide in the presence of peroxyulfuric acids was also discussed by Isida and Yukawa (33) and by Denisov (34).

A sensitive and accurate volumetric method, due to Knecht and Hibbert (54) employs a dilute solution of titanous chloride,  $TiCl_3$ , which when added to an acidified solution containing hydrogen peroxide, causes a change of color to yellow, then to deep orange (peroxytitanic acid), finally to colorless, as the peroxy acid is reduced to titanium dioxide. The method is applicable even in the presence of organic substances but the titer of the titanous chloride solution must be continually checked by means of a solution of ferric chloride, prepared in turn from a known quantity of ferrous ammonium sulfate. However, Tritton (55) found the titanous chloride method inferior to the permanganate or iodimetric methods.

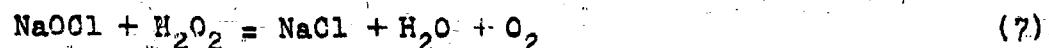
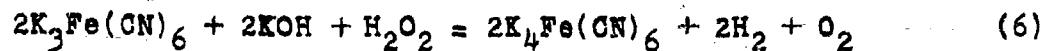
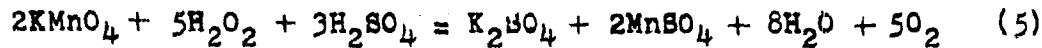
The titanous chloride method may also be applied colorimetrically, and is most effective in this case for determining small quantities of hydrogen peroxide when present in highly colored solutions, where color changes can be determined accurately. The method, referred to below (under Colorimetric Methods) is discussed by Reichert, McNeight and Reidel (47), together with an account of various other methods for the determination of hydrogen peroxide.

#### Gasometric Methods

These methods are based upon the measurement of the volume of oxygen from a known quantity of a solution of hydrogen peroxide, either by the catalyzed decomposition of the peroxide:



or by interaction with an oxidizing agent such as an acid permanganate, alkaline ferricyanide, or neutral sodium hypochlorite (56) solution:



In the catalytic decomposition process it will be noted that one mole of hydrogen peroxide yields but half a mole of oxygen, whereas the reactions of hydrogen peroxide with oxidizing agents results in a 1:1 molar relationship between hydrogen peroxide and resulting oxygen.

In the catalytic process the hydrogen peroxide present in the sample may be decomposed with the assistance of finely divided platinum or silver or of colloidal solutions of these metals, or of solid manganese dioxide; the volume of oxygen liberated being measured in a suitable gas volumetric apparatus. Catalase is often used in biochemical work (57).

Whether the oxygen is derived directly from the catalyzed decomposition of hydrogen peroxide or from interaction of hydrogen peroxide with an oxidizer, the results are subject to two sources of error, namely, the solubility of oxygen in water and the possibility of supersaturation of dissolved oxygen in the solution employed or in the confining liquid of the gas measuring apparatus. If a mercury burette is employed, a milliliter or two of water, saturated with oxygen, may be placed above the mercury meniscus in the burette, so that the oxygen collected may be brought to saturation with water vapor at the temperature of the burette. One form of an apparatus for gasometric analysis is depicted in Chapter 9. Matsuura (58) proposed to determine the gas evolved from hydrogen peroxide decomposition by measuring the amount of foam (stabilized with saponin) developed. For everyday practice,

the gasometric method is not frequently resorted to, being less convenient than some of the alternative procedures.

#### Colorimetric Methods

The content of hydrogen peroxide in very dilute solutions has been estimated by several colorimetric methods. For example, the color produced when a starch-potassium iodide mixture is allowed to react with the sample containing hydrogen peroxide may be used, within certain limits, to serve as an index of the peroxide content of the sample (59). Although of apparently high sensitivity, such a method is open to some uncertainty, for it is familiar that dilute solutions of hydrogen peroxide react but slowly with potassium iodide; and, on the other hand, prolonged standing in contact with air will bring about some oxidation of iodide ion to free iodine. The range of concentration of hydrogen peroxide over which the potassium iodide method is applicable is from about 0.08 mg per liter to about 0.5 mg per liter. The increase in intensity of the blue color imparted to starch by iodine when more than 1 mg per liter of iodine is liberated cannot be followed quantitatively.

The reaction of peroxide with iodide ion, followed by spectrophotometry of the resulting iodine solution at 350 millimicrons has been found capable of detecting as little as 0.3 p.p.m. of hydrogen peroxide (60).

Less sensitive is the colorimetric estimation of the red color of ferric thiocyanate resulting from reaction of ferrous sulfate solution with hydrogen peroxide in the presence of ammonium thiocyanate (61). The lower limit of sensitivity here appears to be about 10 p.p.m. of hydrogen peroxide. If the solution is clear and otherwise transparent to ultraviolet light, direct spectrophotometry may be carried out on hydrogen peroxide solutions at concentrations as low as about 8 p.p.m. hydrogen peroxide (62).

The peroxytitanic acid test has been adapted to a colorimetric procedure for the determination of small quantities of hydrogen peroxide in aqueous solution (63). The reagent solution

employed by Bonét-Maury (60) consisted of 10 g of  $Ti(SO_4)_2$ , 50 ml of water and 20 g conc. sulfuric acid, and was allowed to stand 24 hrs and centrifuged to clarify the solution.\* One drop of the reagent added per ml of solution tested developed a color which was measured in a photoelectric colorimeter and compared with a curve constructed from known quantities of hydrogen peroxide. As little as 0.1 mg of hydrogen peroxide per liter is said to be detected in this way.

Somewhat less sensitive than the  $Ti(SO_4)_2$  reagent, a solution of vanadium pentoxide in concentrated sulfuric acid has also been used for the detection of hydrogen peroxide (62). The color change is from green to brown.

Aminopyrine (65) has also been proposed for the colorimetric determination of hydrogen peroxide.

#### Other Methods of Analysis

Several other methods, particularly adapted to the microdetermination of hydrogen peroxide, may be mentioned which involve points of interest.

Musha, Higashino and Doi (66) describe the use of ferron reagent,\*\* which forms a dark green complex with ferric ion, but not with ferrous ion, in the microdetermination of hydrogen peroxide. The amount of  $Fe^{+++}$  produced by oxidation of  $Fe^{++}$  by hydrogen peroxide is determined and the corresponding amount of hydrogen peroxide may then be calculated. Ions of heavy metals interfere as well as anions of oxidizing or reducing character.

The polarographic microdetermination of hydrogen peroxide (67, 68, 69, 70, 71) depends upon the fact that when oxygen dissolves in water the polaragram obtained shows two

\* A  $Ti(SO_4)_2$  test solution may also be prepared according to M. Eisenberg (64) by dissolving 1 g  $TiO_2$  in 100 ml conc.  $H_2SO_4$  by heating 15 hrs at 150°C, cooling and diluting with 400 ml of water.

\*\* Ferron is 7-iodo-8-quinolinol-5-sulfonic acid.

plateaus, one due to reduction to the peroxide state, the second to reduction of the peroxide. As little as 1 γ in a 2 ml sample is said to be detected by this method.

Giguère and Jaillet (68) also studied the polarographic analysis of dilute hydrogen peroxide solutions especially with the purpose of ascertaining the applicability of the dropping mercury electrode with a stationary platinum electrode to the continuous analysis of flowing solutions; and concluded that for this purpose solid microelectrodes were of little value. The polarographic method has also been applied as a control of purity of hydrogen peroxide solutions by the detection of the presence of such impurities as iron, lead and copper compounds (69), as well as to the determination of the content of stabilizers, such as stannate. Reimers (72) developed a polarographic method for the detection of hydrogen peroxide in the presence of ether peroxide.

#### Physical Methods of Analysis

For the routine determination of hydrogen peroxide in aqueous solutions, and in the absence of other solutes, recourse may be taken to purely physical methods of determination, such as measurement of the refractive index or density of the solution. The refractive index of the solution may be quickly measured, as with a dipping refractometer, and the concentration of the peroxide determined by reference to available tables (73). The results are said to compare favorably with those obtained by titration methods. The obvious advantages of convenience and speed in this method with the dipping refractometer are in part offset by the expense of the equipment required and the fact that a relatively large sample is necessary. If the more convenient Abbe refractometer, which requires only a small sample, is used there enter the problems of careful control of temperature as well as protection against catalytic decomposition of the hydrogen peroxide sample.

Again, in the case of pure aqueous solutions of hydrogen peroxide, the determination of the density of the solution

offers a direct measure of the concentration of the solution. Data such as that given by Huckaba and Keyes (74) or the Data Book of Becco Sales Corp. may be employed for this purpose (see also Chapter 5). It is necessary to observe that in the determination of density, either pycnometrically or by means of a hydrometer, formation of bubbles of oxygen, caused by decomposition of the peroxide, may introduce appreciable error (75).

Infrared absorption by hydrogen peroxide is not sufficiently strong to serve as a satisfactory basis for a method of analysis. Ultraviolet absorption by hydrogen peroxide is strong, and, although Beer's law does not hold strictly, reasonable accuracy may nevertheless be achieved by this means. The method is especially applicable to the analysis of vapors (see Chapter 5). Other physical properties have been little used for the analysis of hydrogen peroxide solutions. Although the dielectric constant would appear to offer an attractive measure of the concentration of peroxide, it could only be used with the purest samples; the presence of electrolytic impurities, which affect the conductivity, has been found to be prohibitive (76). Galvanic cells have been proposed (77) for the detection of hydrogen peroxide.

#### DETERMINATION OF ADDITIVES OR CONTAMINANTS IN HYDROGEN PEROXIDE SOLUTIONS

It is sometimes of considerable importance to establish, qualitatively or quantitatively, the presence in hydrogen peroxide solutions of small concentrations of various additives such as stabilizers, or contaminants, especially of catalytic metal ions. It has been indicated above that polarography may be useful in this regard (69); for example, in the detection of the presence of such catalytic ions as ferric, cupric and lead ions, or in the establishment of the presence of stannate stabilizer. Alternatively, a sufficiently large sample may be evaporated and/or decomposed, under conditions such that the container may contribute only a minimum of material (and that of known

composition\*) to the residue obtained, which is then examined spectroscopically. If decomposition of the hydrogen peroxide sample is permitted to occur during the evaporation of the solution, care must be taken that the spray attending the decomposition does not entrain sizable quantities of the dissolved material, which then will be lost from the final residue to be submitted for analysis.

Such a non-volatile residue may be expected to vary somewhat with the concentration of the peroxide solution employed. In the case of a 3% solution, the U. S. Pharmacopoeia XIV, p. 286, specifies that a non-volatile residue, obtained by evaporating 20 cc of the solution to dryness on a water bath, followed by drying at 105° for 1 hour, should not exceed 30 mg. Heavy metals should be present in amounts not exceeding 5 p.p.m., and the arsenic content should be less than 2 p.p.m. A limit of 500 p.p.m. is placed on the preservative used in stabilizing the solution. The acidity of the solution should be such that not over 2.5 ml of 0.1 N sodium hydroxide is required to neutralize 25 cc of the peroxide solution. Slightly different limits are set for 30% hydrogen peroxide in the specifications given by the American Chemical Society (78) for reagent chemicals. Procedures are given (78) for testing for organic residue, nitrate, chloride, phosphate (79), sulfate, ammonium, heavy metals, and iron. Fluoride and oxalate also are sometimes determined. Determination of silica in hydrogen peroxide (80) is of importance in bleaching operations.

\* It is clear that even if the container consists of such inert materials as high-purity aluminum or a borosilicate glass, some slight pick-up of these materials by the solution is inevitable.

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## CHAPTER ELEVEN

### USES

The first commercial uses of hydrogen peroxide were as an antiseptic and as a bleaching agent, particularly for substances of animal origin such as hair and wool, which are easily harmed by other bleaching agents. However, until 1910, hydrogen peroxide was manufactured exclusively from barium peroxide and the low stability of the product plus the high cost associated with handling and transporting the low concentrations produced (up to about 5 wt. %) severely limited its applications. The electrolytic processes,

which largely supplanted the barium peroxide processes in the major industrial nations during the period 1910-1925, involve vaporization of hydrogen peroxide as it is formed by hydrolysis of a peroxy compound, followed by fractional condensation of the product. As a consequence, a much purer product of higher stability and higher concentration was produced which led to increasing acceptance. In non-military applications, the principal consumption of hydrogen peroxide has been and continues to be as a bleaching agent. Substances of animal origin are most commonly bleached with hydrogen peroxide. In the bleaching of cellulosic materials, hydrogen peroxide has been gradually replacing or supplementing use of hypochlorites. Thus in 1952 most of the bleached cotton cloth in the United States had been treated with hydrogen peroxide, either as the sole bleaching agent, or as an antichlor following hypochlorite bleaching. In the last few years there has developed considerable use of sodium peroxide and hydrogen peroxide in the bleaching of groundwood and to some extent to supplement use of chlorine and hypochlorite in bleaching of chemical pulp. Increasing amounts are also being consumed in the manufacture of organic chemicals. Very large quantities of concentrated hydrogen peroxide were used during World War II, particularly by Germany, as a

propellant. These and other uses are discussed in more detail below.

Figures on the world and United States production of hydrogen peroxide are given in Chapter 3. United States production in 1951 was approximately three times that in 1945 and about ten times that in the period 1915-1930. Little quantitative information is available on the end-use of hydrogen peroxide. A U. S. Department of Commerce report in 1947 (1) gave the following relative distribution of uses of hydrogen peroxide in the United States during World War II.

TABLE 1

**RELATIVE USES OF HYDROGEN PEROXIDE  
IN THE UNITED STATES, 1944-45**

**Non-Military**

Textiles	35.3
Chemical Processing	9.3
Resale and small orders	13.0
Miscellaneous	8.5
Drugs & Cosmetics	3.9
<b>Total of Non-military uses</b>	<b>70.0</b>
<b>Military</b>	<b>30.0</b>

The classifications are somewhat vague but it is indicated that the textile industry is the most important non-military consumer of hydrogen peroxide.

Another report in 1946 (2) indicated that at that time 20 - 30% of the bleached cotton was bleached by hydrogen peroxide, 65 - 75% by hypochlorite and about 5% by both. However it is known that the introduction of continuous bleaching processes using hydrogen peroxide, particularly since 1946, has displaced most of the use of hypochlorite indicated above. In the United States, the amount of hydrogen peroxide consumed in the bleaching of wool is small relative to its use with cotton, although the opposite is true in Great Britain. The distribution of uses of hydrogen peroxide during recent years has been estimated by

Kauffmann (3) to be approximately as follows:

TABLE 2

## DISTRIBUTION OF USES OF HYDROGEN PEROXIDE

Consumed By:	<u>1947</u>	<u>1949</u>	<u>1951</u>
Textile Industry	70%	60%	55%
Other Industry	30%	40%	45%
Consumed For:			
Bleaching	78%	80%	70%
Other Purposes	22%	20%	30%

Imports of hydrogen peroxide into the United States have been relatively minor in amount, for at least the last twenty or more years. For example, during the recent period of 1946 - 1949, the value of hydrogen peroxide imports was less than \$25,000 per year, as indicated by the fact that hydrogen peroxide was not listed in the U. S. Bureau of Census report covering this period.

The 1952 U. S. selling prices for hydrogen peroxide in commercial quantities are quoted in Table 3 (4).

TABLE 3

## SELLING PRICES OF HYDROGEN PEROXIDE, 1952

Cone., wt. %	Price per pound of aqueous solution	Price per pound of contained H <sub>2</sub> O <sub>2</sub>
3	\$0.037 - 0.05	\$1.25 - 1.66
27.5	0.175 - 0.195	0.635 - 0.705
35	0.207 - 0.235	0.595 - 0.67
90	0.67 - 0.75	0.745 - 0.835

The average selling price of 27 - 35 wt. % hydrogen peroxide solutions at New York has varied between \$0.55 and \$0.70 per pound of contained hydrogen peroxide during the period 1940 - 1953. The U. S. Census of Manufacturers for 1947 quotes the value at the plant of 27.5% solution as \$0.515 per pound of contained hydrogen peroxide.

The various applications of hydrogen peroxide are based upon several important properties, as follows:

(1) Oxidizing agent. In this capacity it serves as

(a) a bleaching agent and antichlor. Since this use accounts for the major portion of hydrogen peroxide consumed, it will be discussed in a separate section from other uses as an oxidizing agent. Other uses are as follows: (b) as an oxidizer for vat dyes, and as a hypo eliminator in photography; (c) in the separation of metals by selective oxidation, (d) as an analytical reagent, (e) as a depolymerizing agent in the modification of resins, adhesives, soluble starch, etc., and (f) in paper de-inking.

(2) Source of Energy. Concentrated solutions of hydrogen peroxide can serve as a highly compact source of energy released either by decomposition or by reaction with a fuel.

(3) Gas Formation on Decomposition. Dilute solutions may be used as a leavening agent in baking and as a foaming agent in the manufacture of porous substances such as foam rubber and porous building materials.

(4) Source of Free Radicals. Hydrogen peroxide and other peroxy compounds are used to initiate polymerization and other reactions involving free radicals.

(5) Effects on Biological Processes.

(6) Use in Chemical Synthesis. As the simplest peroxide compound, hydrogen peroxide is the starting material for preparation of most of the inorganic and organic peroxy compounds and also has a number of uses as a reagent in organic chemical synthesis.

These applications will be discussed in detail in the above order. Hydrogen peroxide also acts as a reducing agent on reaction with a few highly oxidized materials such as permanganates, dichromates and ceric salts, in which all the oxygen gas formed comes from the hydrogen peroxide. However, these reactions

have no significant commercial application; they are discussed in Chapter 7, Chemical Properties.

A considerable degree of interchangeability exists between hydrogen peroxide and various other peroxy compounds in their use in an aqueous medium. Thus in those cases in which hydrogen peroxide or  $\text{HO}_2^-$  ion is the active specie hydrogen peroxide may be added as such and the pH adjusted to the appropriate value, or the hydrogen peroxide may be formed in situ from another peroxy compound by hydrolysis or neutralization, e.g., of sodium peroxide, or from a salt containing hydrogen peroxide of crystallization. Conversely the active specie may actually be a more complex peroxy compound, such as peroxyacetic acid, which likewise can be added as such or else formed in situ from acetic acid and hydrogen peroxide. With a few exceptions, other peroxy compounds are all prepared from hydrogen peroxide, as discussed at the end of this chapter.

The discussion below does not include all the uses for the various peroxy compounds, but is restricted to those applications in which hydrogen peroxide as such is used, or has been considered for use.

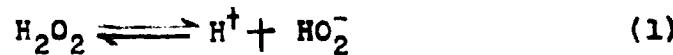
#### BLEACHING

The primary consumption of hydrogen peroxide is as a bleaching agent. The action desired is that of destroying or bleaching colored matter or converting it into a form which is soluble in water or in the bleaching agent. A bleach may be either a reducing agent, such as sulfur dioxide, hydrosulfites and thiosulfates or, more commonly, an oxidizing agent such as a peroxy compound, chlorine, or oxygen-containing chlorine compounds such as hypochlorites, sodium chlorite and chlorine dioxide. Dichromates, ozone and permanganates have also been used to a slight extent as bleaches. In the latter case the manganese dioxide formed is removed by subsequent treatment with hydrogen peroxide, acetic acid or oxalic acid. Of the other peroxy compounds which are also used as bleaching agents, sodium peroxide

may be applied instead of or with hydrogen peroxide in wood pulp bleaching and paper de-inking. Sodium peroxyborate is sometimes used in commercial laundries where a mild bleaching agent is desired, or in situations where bleaching is done occasionally or in small volumes. Its use as a "dry bleach" in home laundries has increased rapidly in the last few years. The aqueous solution of peroxyborate gives in effect a solution of hydrogen peroxide buffered at about pH = 10.

The choice of the bleaching agent for a given application rests upon such factors as relative costs of the chemicals and of the bleaching operations, efficacy of the agents, stability, corrosiveness and handling problems, degree of reduction of strength of the treated material, permanency of the bleaching action, the ease with which the bleached material may be dyed or printed, and also on other less tangible effects such as the "hand" and appearance of the bleached material, particularly in the case of textiles. In some cases, such as with cotton textiles, the material is first treated with an alkali or an acid and the total operation is regarded not only as a bleaching process but also as a general purification to remove such substances as starches, fats and waxes, and seed husks or other residues, which might remain in the woven fibre.

Little is known of the nature of the chemical reactions whereby peroxides destroy colored material. The rate at which hydrogen peroxide bleaches a given substance increases with pH, from which it is inferred that the active species is perhydroxyl ion,  $\text{HO}_2^-$ , which is formed by ionization of hydrogen peroxide.



Increasing the alkalinity of a peroxide solution decreases the hydrogen ion concentration and increases that of the perhydroxyl ion. It is well established that the oxygen released by decomposition of a peroxide in general has no bleaching action and may, in fact, be harmful. For example,

cellulosic materials in strongly alkaline media are slowly attacked by oxygen with reduction in chain length of the cellulose molecules and accompanying loss in strength. Therefore bleaching operations should be so designed as to minimize decomposition of peroxide into oxygen as is caused, for example, by minute amounts of metals such as iron, copper and manganese.

The various kinds of materials which are bleached are logically divided into those consisting primarily of cellulose in contrast with those primarily of protein structure.

#### Bleaching of Cellulosic Materials

Textiles. Essentially all cellulosic fibres, such as cotton, linen, jute and rayon are bleached with either chlorine compounds or hydrogen peroxide or both. Until the 1930's either calcium hypochlorite or sodium hypochlorite was the usual agent used, because of the relatively higher cost of hydrogen peroxide, per unit of bleaching power, and the lack of knowledge concerning methods of keeping it sufficiently stable in storage and use. In 1952 chemical costs were approximately \$2.50 - \$3.50 for peroxide treatment as compared with \$1.50 - \$2.50 for hypochlorite treatment, per thousand pounds of cotton goods. However, hypochlorite had been largely replaced due to improvements in techniques of stabilizing and handling hydrogen peroxide and acquisition of experience which showed the following:

1. Hypochlorite is a more vigorous oxidizing agent than hydrogen peroxide. Although equal degrees of whiteness with minimum loss in fibre tensile strength can be achieved with either bleaching agent, more careful control is required to achieve this with hypochlorite than with hydrogen peroxide. With peroxide, there is less possibility of fibre degradation and loss of strength by over bleaching.

2. The fact that the decomposition products of hydrogen peroxide are oxygen and water simplifies necessary treatment subsequent to bleaching.

3. Starting about 1940, two large producers of hydrogen

peroxide in the United States, the Buffalo Electro-Chemical and the duPont Co., began to introduce continuous processes using hydrogen peroxide for large-scale bleaching operations (e.g., 400,000 yards or more in a 120-hour week). Although the capital investment for this equipment is high, it has smaller space requirements, labor costs are lower, and the process uses less steam, water and chemicals than batch processes using hydrogen peroxide.

4. The suitability of hydrogen peroxide for all fibres makes it possible to use the same equipment for various textiles.

5. Hydrogen peroxide may be used to bleach goods containing vat and other dyed yarns which would be harmed by chlorine bleaches.

6. Peroxide-bleached cotton has good absorbency, a soft "hand," and a more permanent white.

In a number of operations, hydrogen peroxide is used as an "antichlor" following bleaching with hypochlorite. Goods bleached with hypochlorite may slowly turn yellow with age. This color change is apparently associated with chloroamines which are formed from hypochlorite and the proteins in the crude cotton fibre. Subsequent treatment with hydrogen peroxide prevents yellowing by destroying the chloroamines, and in so doing has less destructive effect on the fibre than an antichlor such as sodium thiosulfate. Depending upon conditions of treatment, the peroxide may also produce a substantial portion of the total bleaching obtained.

The techniques used for bleaching cellulosic fibres may vary considerably with each different material, and usually must be developed by more or less empirical methods for any new substance. Literally hundreds of different recipes have been published for bleaching various substances, differing in such variables as time, temperature, concentrations, stabilizing agents, and kinds of preliminary and successive treatments. Only a few typical techniques can be given here.

The most important characteristics of the material to be bleached which determine its treatment are the cellulose content and the amount of lignin present. Pure cellulose is relatively inert to alkali in the absence of oxygen, but lignin and lower molecular weight cellulosic-type materials such as the hemi-celluloses are readily attacked. Thus, the allowable severity of the treatment of the fibre depends upon the extent to which lignin and other non-cellulosic materials are present and act as cementing and strengthening agents to the fibre. For example, cotton, which is a highly pure form of cellulose, can be treated at elevated temperature with caustic soda to remove foreign impurities, such as waxes, without affecting the fibre strength, and it can be bleached with hydrogen peroxide under relatively severe conditions, such as pH values up to about 11 and boiling temperatures. Slater and Richmond (5) classify vegetable fibres other than cotton into three groups according to their cellulose content and the gentleness of the treatment necessary, as follows: (I.) Fibres containing over 85% cellulose and low in lignin or pectous cementing materials, e.g. flax. (II.) Fibres with cellulose content less than 85% and lignin content between 6 and 18%; e.g. jute, sisal, or phormium tenax. (III.) Fibres with exceptionally high lignin content, e.g. coir, with 34% lignin content.

Bleaching of materials which contain any appreciable amount of lignin or other non-cellulosic substances is commonly carried out by treatment first with hypochlorite followed by treatment with hydrogen peroxide. A typical bleaching operation for linen yarn is an example of that used for group I substances (5). The linen is first boiled at 212°F for about 3 hours, using sodium carbonate instead of the sodium hydroxide used with cotton. This is followed by treatment with dilute calcium hypochlorite having 5.6 g of active chlorine per liter, washing with 0.1 - 0.2% sulfuric acid and then soaking for 4 - 5 hours in a solution at 160 - 170°F containing about 0.1 - 0.2% H<sub>2</sub>O<sub>2</sub> in addition to sodium carbonate and sodium silicate. If the linen is bleached to a full white, the fibre is substantially weakened and there-

fore partly-bleached grades are frequently produced and sold as such. In jute, a group II material, the cellulose fibres are relatively short (2 - 5 mm) and are cemented together by the lignin and hemicellulose which, although having little tensile strength by themselves, are responsible for most of the mechanical strength of the fibre. Since they are more readily attacked than cellulose, the bleaching and other treatments must be less severe than those used for cotton or group I materials. A typical treatment for jute yarn would be a short immersion in calcium hypochlorite containing 2.5 - 3.0 gm of active chlorine per liter plus 0.7 gm of sodium carbonate per liter, followed by bleaching with the same peroxide solution specified above, but for 1.5 to 2 hours. A bleaching treatment recommended for coir is as above, except that a preliminary treatment with bisulfite is required, plus a final treatment with sodium hydrosulphite.

Synthetic cellulose fibres, such as viscose rayon and cellulose acetate, require fairly mild bleaching conditions. Acetate rayon in particular is subject to hydrolysis at high pH values. A typical bleaching operation would consist of immersion for 30 - 45 minutes in a bath containing 0.1 - 0.2% hydrogen peroxide, plus appropriate stabilizers, the bath being held at 160 - 180°F and at a pH of 8.8 - 9.5.

The major consumption of hydrogen peroxide in textile operations is in bleaching cotton. Cotton may be treated in a wide variety of forms such as yarn, piece goods, or finished materials in batch-type operations, or in rope or open width form in continuous bleaching lines. Batch operations are usually carried out in cement-lined iron kettles called kiers or in vats or tanks preferably made of stainless steel. Tile linings may crack at the higher bleaching temperatures. Preliminary treatment of the cotton varies, but always involves thorough cleaning and purification. A typical hydrogen peroxide bleaching solution will contain 0.1 - 0.4 wt. % hydrogen peroxide, about 1% to 1.5% sodium silicate, and sufficient sodium hydroxide to bring the pH to 10.5 - 11.5. In batch

80.

operations, the cloth will be treated with this solution for 2 - 8 hours at 175 - 212°F, usually using some form of agitation. For bleaching naphthol-dyed goods a pH of 7.0 - 9.0 is used to avoid attack on the dye. Most of the cotton bleached in the United States is now treated by a continuous process. In a typical installation the cleaned cotton goods are saturated with a 3 - 4% sodium hydroxide solution and then passed continuously into the top of a hollow box shaped like the letter J, which holds the cloth for a residence time of 1 to 1½ hours, during which it is steamed at 212°F. The cloth is continuously removed from the bottom of the J-box, is washed, saturated with a bleaching solution containing about 0.2 - 0.5% hydrogen peroxide, 1% to 1½% sodium silicate, and 0.05 to 0.25% sodium hydroxide to give a pH of about 10.5, and then steamed for about 1 hour at 210 - 212°F in a second J-box. Operating speeds of 80 to 300 yards per minute have been quoted.

The role of sodium silicate, which is commonly added to the bleaching solution, is many-fold. It acts as a stabilizer to reduce wasteful decomposition of Hydrogen peroxide and also as a buffer to hold the pH at the desired level. In addition it has some detergent and penetrant powers and also inhibits corrosion of metal equipment. The optimum pH is set by a balance between two extremes; at high pH values (above about 11.5), rapid bleaching occurs, but the hydrogen peroxide rapidly decomposes and close control is also necessary to attain proper bleaching without fibre damage. At substantially lower pH values, the rate of bleaching becomes uneconomically slow.

A valuable bibliography recently appeared (6) prepared by a committee of the American Association of Textile Chemists and Colorists. It gives brief abstracts of all articles which were published on textile bleaching during the period 1900 - 1950. It lists 245 references pertaining to peroxide bleaching, 153 on hypochlorite bleaching, including

a number referring to both peroxide and hypochlorite, and 321 on other chemical agents used in bleaching processes, apparatus, etc. More detailed information on techniques of cellulose textile bleaching may be obtained from these references, from various hydrogen peroxide manufacturers (7 - 10), or from books on cellulose and cotton (11, 12).

The bleaching action of hydrogen peroxide also finds use as a stain remover and laundry bleach in the home. A 20 to 1 dilution of 3% hydrogen peroxide in lukewarm, soapy or clear water to which some ammonia has been added and in which clothes are soaked for 30 minutes, rinsed, and dried, imparts the advantages of peroxide bleaching to the home laundry (13). The price differential and necessity for using two fluids has kept hydrogen peroxide from competition with household hypochlorite-type bleaches, but powdered bleaches based on sodium perborate offset the handling disadvantages and have been well received in spite of their higher cost.

Wood Pulp Bleaching. Wood consists of about 45 - 55% cellulose; the remainder consists of carbohydrates such as pentosans and hemicelluloses, and non-carbohydrates such as resins, fats, waxes, lignin, tannins and ash.

Paper and paper products are made from two general kinds of wood pulp. Mechanical pulp, or groundwood, is made by mechanical disintegration of the wood, after removing the bark, and contains essentially all of the components originally present. Paper containing mechanical pulp deteriorates rapidly, particularly in contact with sunlight and air, because of the lignin and other relatively unstable materials present. Paper products of much higher stability can be made from chemical pulp, in which essentially all of the non-carbohydrate components of the wood have been removed by a "cooking" process and subsequent bleaching operations. Pulps of intermediate composition, produced by less complete treatment and known as semichemical and chemigroundwood pulps, are also manufactured to some extent. Three chemical processes are used for lignin removal: (a) The sulfite process

uses a hot aqueous solution consisting of sulfur dioxide plus calcium bisulfite or magnesium bisulfite. It is usually applied to coniferous woods such as spruce and hemlock. (b) The soda process uses a sodium hydroxide solution and is usually applied to deciduous woods such as poplar. (c) The sulfate (Kraft) process uses a solution of sodium hydroxide and sodium sulfide. It is applied particularly to pine and other very resinous woods. The product is strong but more difficult to bleach.

In each of these chemical pulping processes it is desired to remove a maximum of the lignous and similar materials, with minimum degradation of the cellulose molecule. This is best accomplished by stopping the cooking process before all of the non-cellulosic material is removed and then subjecting the pulp to a purification and bleaching operation. The purposes of this subsequent treatment are therefore to continue the removal of non-cellulosic material and to destroy colored material retained by the fibre. This is usually accomplished by one of two methods: (a) Treatment with a hypochlorite solution (either calcium hypochlorite, or else sodium hypochlorite made by reacting the calcium salt with sodium carbonate or sodium hydroxide), which has a pH of 8 - 11 in the presence of the pulp, produces a cream-colored paper. (b) In the so-called two-stage or multi-stage treatment the pulp is first contacted with an aqueous chlorine solution. (Chlorine disproportionates in water to form hypochlorous and hydrochloric acids and gives a pH below 2.) The pulp is then neutralized with calcium hydroxide or sodium hydroxide, which extracts material made soluble by the chlorine. This is followed by treatment with hypochlorite or peroxide. The chlorine and alkaline wash reduce the color relatively little and are generally regarded as a purification step. Subsequent bleaching is particularly effective after such purification. The alternate chlorine and alkaline treatments may be repeated two or three times before the bleaching stage in order to secure a desired whiteness. The amount and type of bleaching done depends upon the characteristics of the wood, the cooking process, and the end-use of the pulp.

Many paper products are made from mixtures of mechanical and chemical pulps so chosen as to achieve at minimum cost, the desired combination of whiteness, durability, printing characteristics, opaqueness, strength, absorbency, etc., set by the end-use requirements. For example, the pulp used for newsprint, in which low cost is the primary factor, consists mostly of groundwood; for high quality book paper, mixtures of chemical pulp are used exclusively. For various items of transitory use, such as magazine, catalogue, wrapping, tissue, and absorbent paper, mixtures of chemical and mechanical pulp are used. The bleaching of all these types of pulp requires much greater amounts of purification and bleaching agents per quantity of material treated than are needed for textiles. Since the chemical cost for hydrogen peroxide or sodium peroxide is greater than for the hypochlorite bleaching solutions, peroxides can be economically used only where the quality of the final product is sufficiently superior to that achieved with hypochlorite to offset the higher cost. The almost infinite number of variations in raw material and desired properties of the final product make each of a variety of bleaching processes appropriate under various circumstances, and make the competitive position of peroxide versus chlorine, hypochlorites and other agents, much more difficult to assess than, for example, in cotton bleaching. It is evident, however, that a particularly important application of peroxides is in the bleaching of groundwood. The most important effect is that peroxides can improve the brightness of groundwood much more than the hypochlorite bleaching agents (by some 10 - 12 G. E. units\*). This makes it possible to incorporate a substantial percentage of this lower-cost pulp in a pulp mixture, termed in the trade a paper "furnish," used in forming printing or tissue papers, and still keep a satisfactory brightness. In addition to its low cost, the mechanical pulp has certain advantages such as in-

\* In North America, paper brightness is conventionally expressed in terms of the degree of reflectivity of light as measured in a standard machine manufactured by the General Electric Company. The reflectance of magnesium oxide is arbitrarily taken as 100%.

creased opaqueness which allows lighter weight paper to be used, and certain desirable printing characteristics, such as bulk resiliency. However, it is important to note that this bleaching treatment does not significantly improve the poor stability of mechanical pulp to sunlight.

By 1950, mechanical pulp was being bleached with hydrogen peroxide or sodium peroxide in 24 mills having a total capacity of 1250 tons/day and mixtures of groundwood and sulfite pulp were being bleached with peroxides in several mills producing a total of about 400 tons/day of printing papers (14). Either hydrogen peroxide or sodium peroxide or a mixture of both may be used. At 1952 market prices, sodium peroxide cost about two-thirds that of hydrogen peroxide, per mole of peroxide ion. To achieve the proper pH in the bleaching bath, sodium peroxide must be partially neutralized with an acid such as sulfuric; on the other hand sodium hydroxide generally must be added to hydrogen peroxide. Consequently the proper ratio mixture of the two peroxides avoids the necessity of using any additional chemicals except stabilizing agents.

The most economic use of peroxides with groundwood is in high consistency systems. The desired alkalinity after adding the groundwood to the bleaching solution is a pH of 10.0 - 10.5, which will drop as bleaching proceeds. Bleaching time depends upon the pulp consistency, temperature, alkalinity, peroxide content, and desired brightness. A typical set of operating conditions is 12% pulp consistency, hydrogen peroxide equal to about 1% of the moisture-free weight of the pulp, plus sodium silicate and/or magnesium sulfate, and a temperature of 100 - 110°F (14). Treatment for about two hours will increase the brightness about 12 G. E. units. Peroxide bleaching may be carried out either batch-wise or continuously in essentially the same equipment as used for hypochlorite bleaching. Another technique used is to apply a peroxide solution to the paper or pulp and allow it to steep at room temperature for one or several days. Thus, the bleaching may be carried out during storage or transportation.

In addition to the usual precautions to avoid peroxide decomposition, bacteria growth must be carefully controlled in groundwood bleaching operations by additions of suitable inhibitors, since many of these produce the enzyme catalase which actively decomposes hydrogen peroxide. Sodium hydrosulfite,  $\text{Na}_2\text{S}_2\text{O}_4$ , is also used for bleaching groundwood; frequently it is used in series with hydrogen peroxide.

Sulfite pulp is also being bleached with peroxides in several mills, in conjunction with hypochlorites, but as yet commercial applications have been limited. Its most common application at present is in the manufacture of speciality papers where extra brightness is required. Here the bleaching with hydrogen peroxide constitutes a final bleaching step after a multi-stage chemical pulp bleaching operation with hypochlorite. The particular advantage here over hypochlorite is the substantially greater brightness attainable without significant degradation, which justifies the extra cost involved. The peroxide treatment also provides improved pulp yields in the bleaching operation, and improved heat stability of the bleached pulp, which is important in the subsequent paper-making operations. Sulfite pulp may also be bleached with hydrogen peroxide in a single stage operation with very high pulp yields. Peroxides can also be used in conjunction with hypochlorite in bleaching Kraft pulp. Here sodium peroxide may be used in the extraction step with sodium hydroxide. In such use, sodium peroxide is cheaper than hydrogen peroxide.

A competitive chemical agent for the final bleaching of chemical pulps is sodium chlorite,  $\text{NaClO}_2$ , which, like peroxides, is relatively expensive but also gives high brightness with low reduction in strength. Sodium chlorite is used in a bath having a pH of about 3 to 5 $\frac{1}{2}$ , under which conditions it slowly evolves chlorine dioxide,  $\text{ClO}_2$ , which is apparently the active agent. Chlorine dioxide can also be used as such, generated externally from sodium chlorite and acid, and then absorbed in water. The disadvantages of chlorine dioxide are

its cost, corrosiveness, and the fact that it is a poisonous gas.

Little attention has been given to study of the mechanism of pulp bleaching by peroxides. In a recent investigation of sodium peroxide bleaching of spruce groundwood, G. W. Jones (15) found that the bleaching caused no pronounced chemical changes in the known components of the groundwood. The lignin was responsible for about 40% and the holocellulose for about 60% of the total peroxide consumed. Methylation of extracted lignin markedly reduced the amount of peroxide consumed in reacting with it, from which it was inferred that the primary peroxide attack in lignin is through carbonyl or possible phenolic hydroxide groups. The characteristics of the reaction between sodium peroxide and extracted lignin suggested that the high efficiency of peroxide bleaching may be due to a high specificity and reactivity of peroxide for the most highly colored lignin fractions.

The use of peroxides in pulp bleaching processes is described in detail in an excellent recent monograph by Beeman and Reichert (14) which also gives some historical background of these processes and extensive literature references through 1950. Further information is available from hydrogen peroxide manufacturers (7, 10, 16), and in numerous patents. Reference (17) lists a number issued in 1949 or later.

Paper De-Inking. Waste paper can be processed by a combination of various mechanical and chemical actions to remove the ink, so that the pulp may be reused in making printing or other light-colored paper. Hot solutions of sodium hydroxide and/or sodium carbonate have usually been used. They attack the various binding materials in the paper and particularly the ink vehicle, and thereby aid in the separation of fibre from the other material present. Alkaline peroxide solutions are more efficacious than a caustic solution of equal pH, and although the cost for chemicals is higher, they permit the utilization of lower grades of waste paper, lower cooking temperatures and give

higher pulp yields and a cleaner product. In addition to its bleaching action, the mechanism of the peroxide action seems to be that of accelerating the hydrolysis and depolymerization of proteins, starches, and oils which are components of the adhesives and of the ink vehicle, thereby solubilizing and loosening the pigments. As in other applications, sodium peroxide and/or hydrogen peroxide may be used, with adjustment to the appropriate pH, and addition of stabilizers. Use of peroxides is of particular interest for de-inking paper containing ground-wood, which is appreciably darkened by ordinary alkaline de-inking solutions.

Bleaching of Other Cellulosic Materials. Other cellulosic materials are bleached with peroxides using techniques similar to those described for cellulose fibres and wood-pulp. Straw bleaching is long and difficult; it requires gentle bleaching and frequently several long successive immersions in peroxide and reducing baths such as solutions of sulfur dioxide or sodium hydrosulfite. Hydrogen peroxide is particularly suitable for bleaching wood, as in the preparation of "blond" furniture, radio and television sets, and baseball bats. In one frequently used method, a 5% sodium hydroxide solution containing sodium silicate is first brushed or sprayed on the wood and after standing, a 27 - 35 wt. % hydrogen peroxide solution is then applied, or the operation is reversed. After the desired bleaching is obtained the alkalinity is neutralized with weak acetic acid and the wood is dried. Alternately the wood may be bleached in a one-step operation using a mixture of peroxide, sodium silicate, and ammonia or sodium hydroxide. Only a thin surface layer is thus bleached, so subsequent finishing operations must be carried out carefully.

#### Bleaching of Protein-containing Materials

Substances of animal origin such as wool, hair, fur, feathers, silk, and leather, are protein in nature and are quickly damaged by strong bleaching solutions or treatment in alkaline media. Consequently for many years they have been bleached

either with a dilute solution of sulfur dioxide or with hydrogen peroxide, or both, with the hydrogen peroxide treatment being used first.

Wool Bleaching. In a typical bleaching operation, woolen blankets are scoured and rinsed and then saturated with a bleaching solution containing about 1.3% hydrogen peroxide, plus sodium silicate to give a pH of 9. Frequently tetrasodium pyrophosphate together with small quantities of ammonia are used instead of sodium silicate. These tend to yield a softer "hand" than does the use of sodium silicate. After squeezing, the blankets are allowed to steep for 24 hours or longer (5) and then washed. Temperatures up to 100 - 120°F can be used for woolen goods, which reduce the bleaching time to 1 - 12 hours with 0.4 - 0.8 wt. % hydrogen peroxide (7, 9, 10). A large fraction of the wool bleached in the United States is treated by a "dry-in" method, applied only to wool stock, in which the scoured wool is immersed in a bleaching solution containing 0.3 - 0.9% hydrogen peroxide at a pH of 3 - 5. After drying, residual hydrogen peroxide must be removed, as by treatment with sodium hydrosulfite or a catalase slurry, to prevent darkening during subsequent dyeing operations (18).

A competitive bleaching agent in laundries is sodium perborate which acts in effect as an alkaline solution of hydrogen peroxide. The bleaching procedure is essentially as described above.

Modification of Wool Properties. Mechanical manipulation of wool while it is moist and hot causes the fibres to coalesce or "felt." Different wools and other animal fibres vary greatly in felting power. In the making of hat felts, the necessary felting properties are frequently imparted by oxidizing the fibre under carefully controlled conditions, known as "carrotting" or "felting." In the past this was done with nitric acid containing a mercury salt as a catalyst but in 1936 it was found that the toxic mercury salt solution could be replaced by a solution of hydrogen peroxide containing a mineral acid (19). The oxidizing action

seems to be that of addition of oxygen to the disulfide groups of the cystine in the wool (20), followed by breakdown of these cystine bridges in the protein structure.

Alkaline solutions of hydrogen peroxide tend to reduce felting and promote shrink-resistance of the wool. Hydrogen peroxide treatments are sometimes used with chlorination treatments of wool in shrink-proofing processes. A recent technical bulletin is available which describes the modification of the properties of wool by treatment with peroxygen compounds and gives extensive literature references to the subject (21).

#### Miscellaneous Bleaching Operations

Hydrogen peroxide has been used for bleaching human hair besides various hair fibres such as those of horses, goats and cows, various furs, feathers and also leather. Small amounts have also been used in bleaching such materials as tripe, bone, pearl and vegetable ivory buttons, glue, headstones, white buck-skin, certain foods, tobacco, cork, sponges and sausage casing. In almost all of these cases mild bleaching processes are required to avoid injury to the material. Fats, oils, waxes, soaps and juices may also be decolorized by the oxidizing action of hydrogen peroxide, although more commonly, colored matter is removed by absorption, as on pulverized diatomaceous earth or activated carbon. Suggested bleaching procedures are usually available for each of these applications (7, 9, 10).

#### **OTHER USES OF HYDROGEN PEROXIDE AS AN OXIDIZING AGENT**

##### In Viscose Rayon Manufacture

Cellulose molecules have a linear polymer structure which may be regarded as consisting of a large number of glucose units, joined end to end by ether linkages. The average chain length is usually determined by measuring the viscosity of a sample dissolved in an aqueous cuprammonium or similar solution; the molecular weight is very nearly proportional to the viscosity. The chain length or molecular weight is commonly ex-

pressed as the degree of polymerization (DP) which is the average number of glucose units per cellulose molecule. The cellulose used for viscose rayon manufacture is usually a specially pure grade of chemical wood pulp and will have initially a degree of polymerization of 800 - 1000. This must be reduced to about 350 so that when subsequently dissolved in a mixture of carbon disulfide and sodium hydroxide to form cellulose xanthate, the viscosity will be sufficiently low to permit satisfactory extrusion through the spinnerette holes. This reduction in chain length is accomplished in U. S. processes by "steeping" the cellulose in sodium hydroxide solution and allowing it to age for 20 - 40 hours under carefully controlled conditions. In an alkaline medium the oxygen present in the air attacks the cellulose chains and reduces the degree of polymerization. (The cellulose is not attacked if oxygen is carefully excluded.) The rate of attack is accelerated by small amounts of polyvalent metal ions such as manganese, iron and nickel which act as promoters. Consequently these impurities must be kept to a minimum to avoid uncontrolled variations in the depolymerization. The time required for depolymerization can be markedly reduced by addition of oxidizing agents, such as hypochlorites or hydrogen peroxide, to the pulp and caustic mixture. Hydrogen peroxide is used for this purpose by some European companies but apparently not in the United States.

The alkali treatment has a number of purposes besides that of reducing average cellulose chain length to the desired degree. It acts as a purifying process to remove other carbohydrates, such as the hemi-celluloses, from the desired  $\alpha$ -cellulose (the most inert of the pulp components), and it also causes a swelling of the cellulose, which is desired before it is converted to the xanthate. The addition of oxidizing agents such as hydrogen peroxide to accelerate the depolymerization does not affect the rate of formation of alkali cellulose or rate of solution of hemi-celluloses (22, 23). Therefore such use has been limited by the complex nature of the various processes occurring and consequent uncertainty as to the effect

that it would have on the properties of the final fibre. It is possible that the accelerating effect of polyvalent metal impurities on the ordinary aging process is through the formation of hydrogen peroxide via autoxidation processes, as discussed in Chapter 2.

The addition of hydrogen peroxide to the cellulose xanthate also accelerates the ripening process used before spinning (24).

#### Hydrogen Peroxide as an Antichlor

Hydrogen peroxide may be used to destroy excess chlorine or compounds containing chlorine which may be left in a substance as a result of a previous treatment. In bleaching operations this may be only one of several functions fulfilled by the hydrogen peroxide, and these applications are described under Bleaching. Hydrogen peroxide has also been considered for use in destroying the chlorine remaining in water after purification. It is proposed to destroy the excess peroxide then remaining by passing the water through a bed of manganese dioxide (25). However the hydrogen peroxide decomposition might cause solution of small amounts of manganese, as discussed in Chapter 8, thus raising the question as to whether the water would be still suitable for human consumption.

#### Oxidation of Dyestuffs

In the application of vat dyes (e.g., the anthraquinone and indigoid group), the insoluble pigment is first reduced to the soluble leuco (colorless) form by a reducing agent, commonly sodium hydrosulfite in an alkaline solution. After the dye is adsorbed on the fibres, it is oxidized, whereby the original insoluble pigment is re-formed and fixed on the cloth. The fact that the pigment is highly insoluble in the oxidized state accounts for the excellent "fastness" of this group of dyes. The oxidation was formerly done with air, but now a chemical bath is usually used. An oxidizing bath typically consists of one of the following: (a) 2 wt. % potassium dichromate plus 2 wt. %

acetic acid; (b) 1 wt. % sodium peroxyborate, or (c) 1 wt. % hydrogen peroxide, with appropriate adjustments of pH and bath temperature (11, 26).

The oxidizing procedure varies with the type of dye and goods, and both continuous and batch operations are used. The use of peroxy compounds here rests on the bright and clear colors obtained, high absorbency of the fabrics, the ease of subsequent washing, and the cleanliness of the operation.

Sulfur dyes, which are extensively used on cotton as rawstock and also on rayon, are reduced, usually with sodium sulfide, and oxidized after application in a similar manner.

In some cases peroxy sulfates may be used as the oxidizer.

The photochemical oxidation and degradation of cotton in moist air is sensitized by most of the yellow, orange and red anthraquinoid vat dyes but not in general by the blue, violet and green group (27, 28). The degradation effect is accompanied by the formation of an oxidizing agent (detected by the starch-iodide test), believed to be hydrogen peroxide and it appears that much of the degradation is caused by hydrogen peroxide attack. Thus a sensitizing dye impregnated on a fibre can cause attack on an adjacent undyed fibre even when there is no contact between them (27). This has been ascribed to volatilization of hydrogen peroxide formed on the dyed fibre with subsequent absorption by the undyed material. Adjacent yarns of nylon or viscose rayon are not significantly affected and there are some indications that degradation of these fibres occurs by other mechanisms. Cotton pigmented with zinc oxide or titanium oxide or with sulfur and basic dyes is also photochemically degraded, although peroxide was not detected with sulfur-dyed fibres. The impregnation of small amounts of metal salts into vat-dyed cotton strongly affects the results. Tests for oxidizing agent showed no diminution in the amount formed after impregnation of the dyed fibres with nickel, some diminution after chromium, more with manganese, and none was detected with copper, iron and

cobalt (28). These results parallel the catalytic activities of these metals for the decomposition of hydrogen peroxide.

The extent of photochemical degradation, however, follows a more complex pattern. Thus the incorporation of copper in the fibre decreases the amount of photochemical degradation of cotton dyed with the most sensitive dyes but increases that of undyed cotton or that treated with the dark-colored vat dyes, so that the amount of degradation becomes essentially independent of the kind of dye used. Iron and other metals also influence photochemical degradation. A possible explanation may lie in the fact that various heavy metals not only decompose hydrogen peroxide but also form it by autoxidation of atmospheric air (see Chapter 2) so that the amount of degradation may become in some cases far more dependent on the nature and amount of heavy metals present than on the nature of the dye. In this connection it would be interesting to study the effects of relatively non-catalytic metals and also of non-metallic catalytic materials on cotton photodegradation.

#### Use in Photography

The action of hydrogen peroxide on photographic emulsions has been discussed in the chapters on formation and chemical properties. The developing action of alkaline hydrogen peroxide described there does not find practical use in photography, being unselective, likely to induce fog, and being far outstripped in efficiency and ease of use by the common organic developers. However, some use has been made of hydrogen peroxide as a developer for blueprints.

Acid hydrogen peroxide containing soluble bromide exerts a reducing effect (in the photographic sense) upon the silver image of a developed plate or print and softens and dissolves the gelatin in the areas where the image exists. This effect has been applied to the production of a gelatin relief which may be used for mechanical reproduction. The process is described by Andreassen (29), Lippo-Cramer (30), and Lange (31).

Hydrogen peroxide alone has not been much used as a general photographic reducer, although ammonium peroxydisulfate is extensively applied for this purpose.

Hydrogen peroxide has been applied in two photographic printing processes (32). In the first of these an ordinary negative is dipped into an etherial solution of a dilute aqueous hydrogen peroxide and put in contact for a short time with a paper coated with gelatin which carries a pigment. This paper is then dipped into a solution of a ferrous salt. The surface of the gelatin-coated paper, which has taken up more hydrogen peroxide from the portions of the negative not carrying an image, now oxidizes the imbibed ferrous salt in proportion to the amount of hydrogen peroxide carried on the various areas of its surface. The ferric salt so formed renders the gelatin insoluble to a greater or lesser depth; on dissolving the soluble gelatin in warm water a print is obtained, carrying the greatest load of pigment in the areas corresponding to the parts of the surface of the negative which carried no image.

The second printing process, known as catatype, is similar with the exception that the gelatin-coated paper carries no pigment. After contact with the negative, the plain gelatin film bearing the absorbed hydrogen peroxide is immersed in a solution of manganous salt or alkaline silver nitrate. The metal is taken up and precipitated as manganese dioxide or silver metal in the areas containing hydrogen peroxide, yielding a positive print.

The power of hydrogen peroxide to produce a latent image in a photographic plate without the action of light has been utilized to obtain directly pictures of the structure of various surfaces. After coating the surface with a solution of hydrogen peroxide, a photographic film is placed in contact with the surface. Certain areas of the surface may decompose more rapidly or absorb more strongly the hydrogen peroxide, and after development of the film such areas show less or no blackening. Kretschmer (33) and Abramson (34) have applied this procedure to obtain

pictures of the skin. The process has also been applied by Kretschmer (35) and Freytag (36) to the study of defects in paper, detection of alteration of documents, and reproduction of printed matter.

Photographic plates or films may be hypersensitized (increased in speed or in sensitivity to a certain region of the spectrum) by bathing in hydrogen peroxide. Schmieschek (37) found that panchromatic plates bathed for five minutes in acid or alkaline 0.075 wt. % hydrogen peroxide solution containing dissolved silver, rinsed, and dried were notably increased in speed and red sensitivity. His recommended formula was: 25% ammonia solution, 1 cc; 30% hydrogen peroxide, 1 cc; water, 400 cc; silver salt, an amount yielding 0.025 g silver. The most satisfactory silver salts were silver molybdate or silver tungstate. These inhibited fogging best, but a number of other silver salts were equally effective in the sensitizing action. The use of hydrogen peroxide for hypersensitization suffers from two drawbacks: the effect varies with the type of emulsion, and treated plates must be used within a short time before fog induced by the treatment becomes noticeable.

Hydrogen peroxide also exerts an intensification action (increase of density or of developability of latent image) on exposed plates. Wightman and Quirk (38) found that treatment with 0.004 to 0.016 wt. % hydrogen peroxide followed by immediate development gave an appreciable intensification; the effect was most pronounced with fast plates and required the presence of soluble bromide for operation. Barnes, Whitehorse and Lawrence (39) studied the effect of various developers on the intensifying action of hydrogen peroxide.

The most common use of hydrogen peroxide in photography is that of hypo eliminator; this was first suggested as early as 1866 by Smith and Spiller (40). Hydrogen peroxide will oxidize to sulfate the thiosulfate remaining in photographic prints after fixing. Thiosulfate or its partially oxidized form, tetrathionate, will react, slowly under ordinary conditions

and rapidly under conditions of high temperature and humidity, with the silver image to form a faded and unsightly brown image of silver sulfide. Removal of the last traces of thiosulfate from papers by washing alone is practically impossible; for permanent prints of the highest quality hypo elimination by chemical means is a necessity.

Crabtree, Eaton and Muehler (41) reviewed the literature and extensively studied the use of hydrogen peroxide as a hypo eliminator. Their recommended formula, known as Kodak HE-1, was as follows: water, 500 cc; 3% hydrogen peroxide, 125 cc; 3% ammonia, 100 cc; water to make 1 liter. Prints are to be washed 30 minutes (1 hour for double weight papers) at 65 - 70°F, immersed in the hypo eliminator for 6 minutes, washed 10 minutes, and dried. The solution will treat fifty 8 x 10 inch prints, or their equivalent, per 4 liters. A slightly different formula is recommended for commercial work.

#### Purification of Metal Salt Solutions

A common problem in the purification of various chemical compounds, particularly metal compounds, is that of removal of iron. This occurs, for example, in processes for obtaining various pure metals and in the purification of electrolytic plating baths. A convenient technique is to add basic substances to a solution to be purified to produce a pH at which ferrous or ferric hydroxide is essentially insoluble but at which the hydroxide of the other metal remains in solution.

The proper pH in each case is set by the degree to which it is desired to eliminate iron, the concentration of the metal desired to be kept in solution, and other factors, such as the amphoteric character of some metals. The pH regions of interest are indicated in Table 4, which shows the maximum pH values at which a solution containing 0.001 gm moles/liter of the metal can exist at room temperature, termed arbitrarily the "precipitation pH." These have been calculated from the solubility product data of Latimer and Hildebrand (42). Obviously the higher the concentration of any individual metal which it is desired to keep in solution, the lower the pH will have to be.

TABLE 4

pH VALUES AT WHICH VARIOUS METAL HYDROXIDES  
FORM A 0.001 MOLAR SATURATED SOLUTION

Metal Hydroxide	"Precipitation pH"
Fe(OH) <sub>3</sub>	2.5
Al(OH) <sub>3</sub>	4.1
Cr(OH) <sub>3</sub>	4.9
Cu(OH) <sub>2</sub>	5.9
Zn(OH) <sub>2</sub>	7.3
Co(OH) <sub>2</sub>	7.6
Pb(OH) <sub>2</sub>	7.7
Fe(OH) <sub>2</sub>	8.1
Mn(OH) <sub>2</sub>	8.4
Ni(OH) <sub>2</sub>	8.6
Mg(OH) <sub>2</sub>	9.9

It is seen that ferric hydroxide is the most readily precipitated; it becomes highly insoluble even in quite acidic solutions. Ferrous hydroxide, however, does not become insoluble unless the solution is essentially neutral, under which conditions many other metals would be also precipitated as the hydroxide, if they are present. Consequently for the complete removal of iron from most metal solutions it is necessary that the ferrous iron be oxidized to ferric. This may be accomplished by blowing the solution with air, but the rate of air oxidation is slow and therefore an oxidizing agent such as hydrogen peroxide or sodium peroxide is sometimes used instead. After oxidation, ferric hydroxide is precipitated by addition of an appropriate base and then it is coagulated by heating and separated by filtering or decanting. It is desirable that the iron be oxidized before the pH is raised in order to reduce the amount of peroxide lost by decomposition, since metals such as iron are more catalytic in the form of the precipitate of oxide or hydroxide than as dissolved ions.

Although in theory the metals having precipitation pH values significantly above ferrous iron could be purified by

this process without first oxidizing ferrous to ferric iron, in practice the separation is easier with previous oxidation. Thus, in the processing of magnesium chloride before electrolysis to magnesium metal, the solution is commonly treated with magnesium oxide to precipitate impurities, but iron removal can be assured by previous oxidation of the solution, as with hydrogen peroxide (43).

Hydrogen peroxide or sodium peroxide have been used for removing the iron from manganese sulfate, nickel sulfate, copper sulfate, zinc chloride, zinc sulfate, and beryllium sulfate (9, 10). Hydrogen peroxide is preferred to sodium peroxide whenever a sodium salt in the product solution may be detrimental. The procedure in general consists of adding a slight stoichiometric excess of the peroxide over the amount of iron present, and then adjusting the pH by addition of a suitable base (frequently the oxide or hydroxide of the metal being treated) and separation of the precipitate. Sometimes more than one metal impurity may be precipitated, as in the purification of lanthanum salts by precipitation of ceric and ferric hydroxide from an appropriate solution (44). In some plating processes the oxidation-precipitation purification with hydrogen peroxide may be carried out in the cell with possible secondary advantages such as prevention of pitting at high current densities. An improvement in the "whiteness" of tin and zinc deposits is also obtained in the presence of hydrogen peroxide.

The fact that the solubility of many polyvalent metal salts changes with the valence state is the basis for several separation procedures involving oxidation with hydrogen peroxide. Thus the coating of iron and steel articles with zinc phosphate is harmed by ferrous phosphate in solution. This can be precipitated, however, by oxidation to ferric phosphate by hydrogen peroxide (45). In recovery operations on non-ferrous scrap, precipitation or solution of tin from the metal salt mixtures can be controlled by oxidation with hydrogen peroxide (46). Competing techniques in metal purification proc-

esses include electrolytic refining, and the use of ion-exchange resins.

Another application of the oxidizing power of hydrogen peroxide is in the regeneration of spent "doctor" solutions in petroleum refineries. The spent sodium plumbite solution is ordinarily converted to lead oxide by blowing with air. It is claimed that addition of hydrogen peroxide during the air regeneration step lowers the total cost by initiating the oxidation and thus reducing the time required and saving steam and power (47).

Moxted (48) has described the revivification of poisoned hydrogenation catalysts with hydrogen peroxide. The action of the hydrogen peroxide is to oxidize the poison on the catalyst, converting it to a "shielded" or non-toxic form. The operation works best through the medium of peroxy acids such as peroxy-molybdate or peroxytungstate or their salts, which can be formed *in situ*. By having present an excess of hydrogen peroxide in the presence of, for example, a molybdenum or tungsten salt, the peroxy compound will be continuously regenerated and the quantity of expensive salt needed thus kept to a minimum.

#### Oxidation of Metal Surfaces

A thin oxide film may be produced on some metal surfaces by treatment with aqueous hydrogen peroxide or peroxide vapor, and several industrial applications of this reaction have been suggested. Thus, ferrous metals may be passivated by heating above the recrystallization temperature in hydrogen and then subjecting to a 20% hydrogen peroxide solution for about 10 minutes (49). In a somewhat similar application, selenium units in rectifiers are oxidized by contact with a spray of aqueous hydrogen peroxide or by air containing about 1 - 10 mg of hydrogen peroxide per liter of air (50). Hydrogen peroxide is also used in a patented method of treating the contact surfaces of copper oxide rectifiers which have been previously oxidized in air (51). The action of hydrogen peroxide to oxidize metal surfaces has also been applied to the making of

100.

accelerated corrosion tests, on aluminum in particular (52). The role of hydrogen peroxide in corrosion is discussed in Chapter 2, under Autoxidation of Metals.

Another use of hydrogen peroxide for the treatment of surfaces may exist in the field of ore flotation. Studies (53) have shown that hydrogen peroxide may alter the surfaces of particles of ore concentrate to improve the selective separation obtained in the flotation process. This action of course depends upon the chemical nature of the ore, for example, Machu (54) cites a case in which the presence of hydrogen peroxide hinders flotation.

#### Hydrogen Peroxide as a Depolarizer

In a number of reactions of solids in liquids in which hydrogen gas is evolved, for example, in the solution of metals in acids or the precipitation of gold from a cyanide solution by zinc, the rate of the reaction is frequently limited by the protective film of hydrogen which forms on the solid. In such cases the rate may be substantially increased by adding to the solution an oxidizing agent (depolarizer) which oxidizes the hydrogen to water and thus permits more rapid contact of reactants. If sufficiently high concentrations of the oxidizer are used, all hydrogen gas evolution on the solid can be prevented. Hydrogen peroxide has been used for this purpose, as well as nitrates and other oxidizing agents (55, 56).

#### Modification of Carbohydrates, Proteins and Gums

Treatment of high polymeric materials like starches, proteins, gums, etc., with hydrogen peroxide or peroxy compounds causes oxidation and depolymerization to occur. The lower average molecular weight of the partially depolymerized products causes them to have a relatively lower viscosity in solution, which makes them easier to solubilize and apply as adhesives, sizings, binders, etc., (9, 57). The depolymerization of cellulose by reaction with peroxide is discussed in Viscose Rayon Manufacture. The mechanism of the depolymerization of cellulose and starches is not well understood, although it is known that

it is preceded and accompanied by an increase in the oxygen content of the cellulose, in the form of carbonyl and carboxylic acid groups (12, 58).

Natural latex may be treated with hydrogen peroxide solutions (using peroxide approximately equal in amount to the dry gum in the latex) to produce adhesive latex and plasticized rubber (59). Treatment with hydrogen peroxide depolymerizes the rubber in the same fashion as does milling, and the products are reported to be nearly identical in chemical and physical properties to those produced in milling. The chemical mechanism is probably the same in both cases, since during the milling (mastication) of rubber in air small amounts of oxygen are absorbed from the air with formation of peroxides, presumably at the unsaturated bonds of the rubber molecules, and this apparently causes rupture of the hydrocarbon chains.

#### Permanent Waving of Hair

The "cold" process of permanent waving of hair involves subjection of the hair to reduction by ammonium thioglycolate solution. The hair is then curled and the wave made permanent by oxidizing the hair with a solution of sodium bromate, sodium peroxyborate or hydrogen peroxide. The peroxy compounds have the disadvantage that they may cause an undesired bleaching of the hair if not properly used; the action of the bromates is satisfactory, but they may cause kidney damage and death if ingested.

#### Applications in Analysis

Hydrogen peroxide is used as an oxidizing agent in a number of analytical procedures, generally where the residues of other oxidizing agents are undesirable or where a peroxy derivative is required. Thus the colors developed by a number of metals in the form of complex peroxy compounds are used as methods of identification or for colorimetric quantitative analysis; for example, the color developed by chromate in the presence of hydrogen peroxide and ether or that of peroxy com-

pounds of vanadium, titanium, molybdenum, cerium and others (60). Procedures using hydrogen peroxide in various analyses are described in books by Feigl (60), Treadwell and Hall (61) and Furman (62). Recent applications of hydrogen peroxide in analytical procedures include the following: The quantitative colorimetric technique for vanadium has been studied in detail by Foster (63). Hydrogen peroxide has been used to determine sulfur in the form of zinc sulfide (64) or sulfur dioxide (65) by oxidation to the sulfate, followed by determination of the sulfate as barium sulfate, or titration of the excess peroxide. Cobalt is precipitated from its solutions by oxidation to the trivalent stage with hydrogen peroxide (66) and similar oxidation techniques may be used for separation of other metals having two or more valence states (see also Purification of Metal Salts). Hydrogen peroxide may also be used in some cases to oxidize and destroy organic material before analysis, as of substances containing phosphorus (67).

Another interesting use of hydrogen peroxide is in the Thomas Autometer used for continuously recording the sulfur dioxide concentration in the atmosphere. An air sample is continuously aspirated through dilute hydrogen peroxide solution, and the increase in electrical conductance, caused by sulfuric acid formation, is recorded as a measure of the sulfur dioxide concentration.

In the Kjeldahl method for the determination of nitrogen, hydrogen peroxide added in the preliminary digestion assists in producing water-clear solutions with a considerable saving of time for the analysis as a whole, and obviates the need for expensive Kjeldahl installations (68).

Addition of excess hydrogen peroxide to acid solutions containing uranium leads to the precipitation of an insoluble peroxide, a fact which has been utilized in the separation of uranium from solution (69).

Most familiar of the analytical uses of hydrogen peroxide is the color reaction with titanium solutions, which serves as the basis for a standard procedure for the determination of this element. Somewhat less familiar is an early method for the

determination of nitrate in the presence of nitrite, which is dependent of the fact that hydrogen peroxide oxidizes nitrous acid rapidly to nitric acid (70).

The yellow color of a peroxidized titanium solution is bleached in the presence of small quantities of fluoride; and a method of determination of fluorine in minerals, based on this effect, was proposed by Steiger (71). The difference in the ease of oxidation of the different halide ions by means of an acidified hydrogen peroxide solution also led Jannasch (72) to devise a method for the determination of iodine in the presence of bromides and chlorides, or of bromine in the presence of chlorides.

Catalase is often determined (73) by its catalytic effect upon hydrogen peroxide. Other procedures using hydrogen peroxide have recently been described for mercury (74), niobium (75), cesium (76) and acetaldehyde (77).

#### USE OF HYDROGEN PEROXIDE AS AN ENERGY SOURCE

Most devices which produce energy by combustion do so by burning a fuel in air. However, there are two circumstances under which it is desirable or necessary to use an oxidant other than air: (1) when power must be produced in a location where air is not readily available, as under water or high above the earth's surface, or (2) when a very high rate of energy release from compact energy sources is desired for a short time, as in a gun propellant, aircraft assisted take-off units or in rockets. Although in some of these cases air could in principle be used by compressing it and storing it in suitable pressure vessels, it is frequently impractical to do so since at all storage pressures approximately four pounds of storage container are needed for each pound of air, compared to one pound or less of container for each pound of a liquid or solid stored. A solid propellant, which incorporates combustible and oxidant in intimate contact, is chosen where the unit is small and emphasis is on simplicity, as in a round of ammunition or a small rocket. More complex

devices are required with liquid propellant systems but they have two pronounced advantages over the solid: (1) the liquid can be carried in a light-weight storage vessel and pumped into a combustion chamber which need be only large enough to provide the desired combustion rate. (Techniques for injecting a solid into a combustion chamber at high pressure are generally unsatisfactory. Consequently the entire solid propellant charge must be initially contained in the combustion chamber, which therefore must be large as well as strong.) (2) The rate of power production can be varied and controlled by regulating the flow of liquid. For these reasons liquid oxidizers and fuels have found application in various relatively large rocket-propelled devices, in underwater propulsion of submarines and torpedoes, and other uses. An ideal liquid oxidant should have many desirable characteristics but three are particularly important: (1) high energy release on reaction, (2) relatively stable to shock and elevated temperatures, and (3) low cost of manufacture. In addition it is desirable that it be non-corrosive, non-toxic, that it react rapidly, and that it have various desirable physical properties such as low freezing point, high boiling point, high density, low viscosity, etc. As a rocket motor propellant, the flame temperature attained and average molecular weight of the combustion products are also particularly important. It is obvious that no one chemical substance will be the ideal oxidant. To the contrary, very few substances have been found to even approach the desired set of characteristics and only three have met with any appreciable application; liquid oxygen, concentrated nitric acid, and concentrated hydrogen peroxide. Hydrogen peroxide has the disability that even in 100% solution, only 47% by weight of the substance is available as oxygen for combustion of a fuel, as compared to 63.5% of nitric acid which is available as oxygen, or 100% if pure oxygen is used. Offsetting this disadvantage, however, is the substantial heat released when hydrogen peroxide is decomposed to water and oxygen. The power or thrust-producing capabilities of these three oxidants in any specified system and with any specified fuel do not vary from one another

by more than 10 - 20%, and a choice among the three for use in a bi-propellant system has therefore been based on other considerations.

Experimental use of hydrogen peroxide as a source of energy was initiated in Germany in 1934 in the search for new sources of power independent of air for the propulsion of under-water craft. This potential military use stimulated the industrial development by E. W. M. in Germany of a concentration process to produce higher strength aqueous solutions which could yet be handled and stored with an acceptably low rate of decomposition. At first a 60% aqueous solution was supplied for military use, but this concentration was later increased until solutions containing up to 85% hydrogen peroxide were made available. The increasing availability of more highly concentrated hydrogen peroxide during the late 1930's in turn led to its application in Germany during World War II for power-production in various other military devices. For example hydrogen peroxide was first used in 1937 in Germany for auxiliary propulsion of an aircraft and in rockets.

An early embodiment of a process for generation of propulsive power from hydrogen peroxide was the scheme of Lysholm (78) which proposed techniques for generating power from the thermal decomposition of hydrogen peroxide, followed by combustion of a fuel with the oxygen generated. However, no actual application of his scheme is known.

Highly concentrated solutions, containing up to 90% hydrogen peroxide, were also produced on a commercial scale at the end of World War II by the Buffalo Electro-Chemical Co., in the United States and B. Laporte, Ltd., in Great Britain.

Concentrated hydrogen peroxide may be used either as a monopropellant, in which it is decomposed under pressure to yield a gaseous mixture of oxygen and superheated steam, or as the oxidant for the burning of a fuel. The monopropellant system is mechanically more simple but less energy can be developed per pound of propellant. In the bi-propellant system, the per-

oxide may be first decomposed and then the fuel burned in the hot decomposition products, or the two liquids may be reacted together directly without previous decomposition of the peroxide. The latter is more simple mechanically but may offer problems in insuring initial ignition and smooth and complete combustion. In each case power or thrust is developed by expansion of the hot gases. The various kinds of rocket power plants based on hydrogen peroxide which were used in Germany during World War II are described in considerable detail by Walter (79) who was closely associated with the development of many of the German military applications of hydrogen peroxide. A number of drawings and photographs are also shown.

A considerable amount of work was done in Germany before and during World War II to develop fuels which would be self-igniting ("hypergolic") with concentrated hydrogen peroxide or nitric acid. The usual criterion of suitability is the minimum time which elapses between contact of the two liquids and appearance of flame (ignition delay). The technique of mixing greatly affects the results, so considerably different conclusions may be reported on the same fuel-oxidant combination by different investigators. The presence of small amounts of certain metal salts in the fuel also may have a powerful effect on reducing the ignition delay, or even in making the system self-igniting at all. In a few of these cases the activity of the metal salt seems to be primarily that of a catalyst which decomposes the hydrogen peroxide and thereby raises the temperature of the system to the ignition point of the fuel; more often, the role of the catalyst is more subtle. Thus suitable catalysts seem to form complexes with the fuel, but the complex must be neither too strong nor too weak. Fuels which have been found to be hypergolic with concentrated hydrogen peroxide fall within one of the following groups of chemical structures: (1) inorganic amines (e.g., hydrazine), particularly in the presence of dissolved copper and iron salts such as potassium cupricyanide and sodium nitroprusside, and also some organic amines such as toluidine and various diamines; (2) compounds having unsaturated bonds

other than those associated with the benzene ring such as (a) several conjugated double bonds, (b) unsaturated bond plus a keto or hydroxy group, (c) unsaturated 5-member ring compounds like furan, pyrrole and cyclopentadiene; (3) aldehydes such as crotonaldehyde; (4) higher aliphatic alcohols and compounds containing hydroxy groups such as pyrocatechol. In each of these cases the effect may be markedly increased by the solution in the fuel of a salt of iron, copper, nickel, vanadium or cobalt. A large amount of detailed information on the German studies is available (80). Broatch (81) recently published a description of an apparatus for measuring ignition delays, including results obtained using 80% hydrogen peroxide as the oxidizer.

The heat of decomposition of aqueous hydrogen peroxides solutions is sufficient under adiabatic conditions to vaporize all the water initially present, plus that formed by the decomposition, if the initial hydrogen peroxide concentration is greater than about 68 wt. %. If conditions are such that all the liquid is vaporized, the final temperature attained is substantially independent of pressure. The adiabatic decomposition temperatures have been calculated for various conditions (82). Figure 1 shows the temperatures which are attained on various degrees of decomposition at 515 psia of concentrated hydrogen peroxide solutions initially at room temperature. The energy which can be developed depends upon the mechanical system employed, the initial and final pressures and the peroxide concentration. As an example, the complete decomposition at 515 psia of 85% hydrogen peroxide in a steady-flow process followed by expansion of the gaseous products through a reversible (100% efficient) work-producing device to 14.7 psia (atmospheric pressure) will produce slightly over 0.1 hp-hour per pound of original solution. Combustion with a fuel such as alcohol or a hydrocarbon before expansion can approximately double the energy developed per pound of fuel plus peroxide solution.

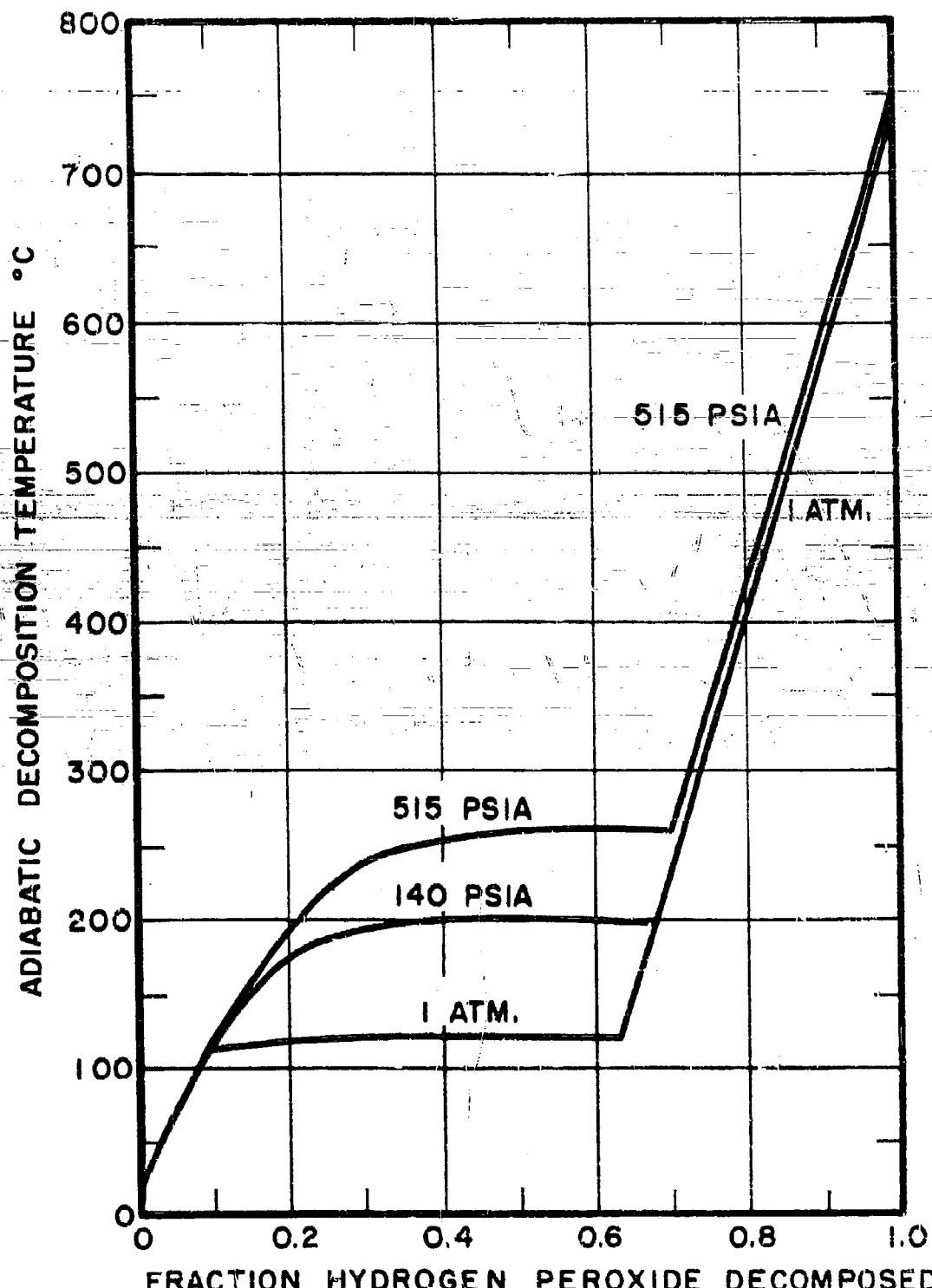


FIG. 1 - EFFECT OF PRESSURE ON THE ADIABATIC DECOMPOSITION TEMPERATURE OF AN AQUEOUS SOLUTION INITIALLY 90 WEIGHT PERCENT HYDROGEN PEROXIDE

Techniques of Decomposition

The production of energy by decomposition of concentrated hydrogen peroxide, either with or without subsequent reaction with a fuel, requires a technique which will give rapid and complete reaction in a minimum volume. Although in principle such decomposition could be obtained by a purely thermal method, as proposed by Lysholm (78), the problems of reliable start-up and operation have always led in practice to the use of catalyst, except where direct reaction with a self-igniting fuel has been used. A number of substances are very active decomposition catalysts, particularly the oxides of various heavy metals. One simple technique is to spray an aqueous solution of a permanganate salt continuously with the hydrogen peroxide solution into a decomposition chamber. The permanganate ion is immediately reduced to form finely divided particles of solid manganese oxides, which constitute the actual catalyst. By using sufficiently fine atomization, as high as 1 kilogram of concentrated hydrogen peroxide can be decomposed per second per liter of volume (79). This technique was used in Germany for catapult launching, and for steam generation to drive the pumps of the V-2 rocket. The solubility in water of permanganate salts increases in the order: potassium, sodium, calcium, and therefore concentrated solutions of either the sodium or the calcium salt were used. Calcium permanganate was of particular value for winter-time use because of the low freezing point of its highly concentrated solutions.

This use of permanganate solutions for peroxide decomposition, however, has not only the disadvantage of the extra complexity associated with handling an additional fluid, but also a continuous stream of solid material is swept along with the steam-oxygen mixture which is highly objectionable if it is to be passed through a turbine. Therefore a number of solid catalysts were developed in Germany which could be packed into a bed into which hydrogen peroxide could be sprayed continuously. A wide variety of catalysts were studied and some specific formulations which

were ultimately used have been reported (83). One type, used in the German hydrogen peroxide-driven submarine, consisted of pyrolusite (naturally-occurring  $MnO_2$ ) mixed with cement and sand, and molded into pellets. In a second type, highly porous porcelain stones were soaked in a mixture of calcium permanganate and potassium chromate and dried. The latter treatment was purported to give longer lasting surface activity. In both cases the particles were 1 - 1.5 cm size. It was reported (79) that in operation at 25 atmospheres pressure 1 kilogram of either of these two kinds of catalyst stones would decompose 150 - 200 gm/sec. of hydrogen peroxide, and that they had a life of about 2000 kilograms of peroxide per kilogram of stone.

Small amounts of impurities in the hydrogen peroxide, either from the manufacturing process or stabilizers purposely added, will gradually reduce the activity of the catalyst. The magnitude of the effect will vary enormously with the nature of the catalyst and the amounts and nature of the materials present in the hydrogen peroxide. Therefore in such applications it is important to use as highly pure hydrogen peroxide as possible, containing the minimum acceptable concentration of stabilizers.

It is evident that the processes occurring in a decomposition chamber are extremely complex, proceeding from a liquid phase reaction at ambient temperature and in concentrated hydrogen peroxide at the inlet, to mixed liquid and gas phase decomposition, to a vapor phase decomposition at high temperature and vanishingly small peroxide concentration at the exit. The theoretical design of such a decomposer was analyzed by Luft (84), making a number of simplifying assumptions, but it is evident that in practice design will be fairly empirical. Luft also describes a number of practical problems which occur in decomposition chamber design and operation. Thus, although a decomposition chamber operates under considerable pressure, it starts up at atmospheric pressure, for which condition a substantially longer bed is required than at higher pressures. Also, the bed is initially cold, and the necessity for high

catalyst activity becomes most acute at the inlet of the chamber and on initiation of reaction. For this reason such stratagems are suggested as the application of a layer of especially active material over the regular catalyst particles, the layer perhaps containing a substance which will dissolve in the initial flow of peroxide and produce rapid homogeneous reaction. This, of course, is only practical for a system which is to be used but once. The initial catalyst zone is subject to high thermal and mechanical stress. Moreover, loss of catalyst activity occurs most readily in this zone during operation by reaction of impurities or stabilizers in the peroxide or by coating of deposits by evaporation. A proposal for overcoming this gradual inactivation is to so construct the catalyst that slow mechanical erosion occurs, thereby continuously making fresh catalyst surface available. However, this is only feasible where the eroded material can be tolerated in the gas stream.

Another problem cited is that of oscillation or pulsations of flow. This can occur if a portion of the bed contains catalyst of low or moderate activity, for example, after a bed has been operated for such a time that the upstream portions of the catalyst have lost much of their activity. A momentary low pressure causes an increased quantity of peroxide to enter and "flood" a portion of the catalyst. This peroxide suddenly decomposes after a very short but finite time interval, suddenly raising the pressure and decreasing the inlet peroxide flow. The subsequent drop in pressure as this gas leaves the chamber in turn allows an increased peroxide flow, and the cycle is repeated. The phenomenon should not occur if the catalyst is all of very high activity, and the oscillating effect will be worse, the lower the catalyst activity, which allows greater peroxide accumulation before the sudden decomposition occurs. A possible corrective measure, besides use of a more active catalyst, is to provide for a higher pressure drop through the nozzles feeding the peroxide to the chamber, or to use other techniques which help divorce the rate of feed from chamber pressure.

The characteristics of liquid and vapor-phase decomposition are considered in Chapter 8.

The various military applications of hydrogen peroxide in Germany will be briefly reviewed below.\*

#### Use in Submarine Propulsion

Before World War II, submarines were conventionally driven by Diesel engines while on the surface and by battery-fed electric motors while submerged. The available capacity and discharge rates of the batteries severely limited the capabilities of the submarine in underwater propulsion. It is particularly desirable for a submarine to have a high underwater speed for escape after attack, but the total energy attainable on rapid discharge of batteries is substantially less than that if they are discharged more slowly. Typical performance of a conventional submarine at the beginning of World War II was that of the German type 7C submarine which had a surface speed of 17 knots and submerged speed of 7.5 knots (85); the latter could be maintained for only a very short time. During the war Germany built the type 21 boat which was capable of a surface speed of 15.5 knots and a submerged speed of 16.5 knots for one hour, obtained by large battery capacity and the use of very thin grids in the batteries.

The use of hydrogen peroxide for submarine propulsion was developed at the Walter Werke, Kiel, where an 80-ton experimental submarine was built before the war and demonstrated a submerged speed of 25 - 26 knots. This was followed by the construction during the war of four school boats and five operational boats, designated as type 17B. These had 380-ton displacement, surface speed of 8.5 knots, and submerged speed of 25 knots. However, they were never put into operational use because of the shortage of hydrogen peroxide. At the end of the war there was under construction a "type 26" boat to have been of 900-ton displacement, 11 knots

\* In a number of descriptions of German work, particularly translations of German documents and other literature not appearing in the usual technical journals, concentrated hydrogen peroxide is referred to under the German military code names of "T-Stoff," "Renal" or "Ingolin."

surface speed and 24 knots submerged speed, with capacity for about 90 tons of hydrogen peroxide--sufficient to maintain the maximum submerged speed for a total of about 6 hours. The peroxide-driven engine was rated at 7500 hp.

The power plant is shown diagrammatically in Figure 2. Concentrated hydrogen peroxide was pumped into a packed catalyst chamber where it was decomposed. The catalyst consisted of porous stones impregnated with a permanganate and allowed to dry. The sodium or calcium salts were preferred for the treatment because of their high solubility in water. Water was also sprayed into the combustion chamber with the fuel (Diesel oil or decalin) in order to lower the temperature of the combustion gases to about 1020°F, the maximum allowable inlet temperature for the turbine. Turbine exit gases were cooled, some of the condensed water recycled to the combustion chamber, and the remainder, plus non-condensable gasses, was pumped overboard. The hydrogen peroxide was stored in collapsible polyvinyl chloride bags outside of the pressure hull. A disadvantage to the peroxide-driven submarine is the quantity and cost of the hydrogen peroxide required. Moreover, other operating characteristics such as cruising radius, space, etc., had to be somewhat sacrificed to obtain the unusual underwater performance. More details of the German peroxide submarines have been published by McKee (85).

Use of atomic energy would presumably permit underwater propulsion for almost unlimited periods. Initiation of the construction of power plants for two atomic-powered submarines had been announced by the United States Navy by 1952. "Jane's Fighting Ships 1950-51" (86) reports that the United States Navy has projected the construction of one atomic-(nuclear-)powered submarine of 2500 tons displacement to cost \$40,000,000, and one submarine of 2200 tons displacement to be powered by hydrogen peroxide in a closed cycle engine, to cost \$37,000,000.

#### Use in Torpedo Propulsion

A torpedo is in effect a miniature, automatically-operated submarine. At the beginning of World War II most opera-

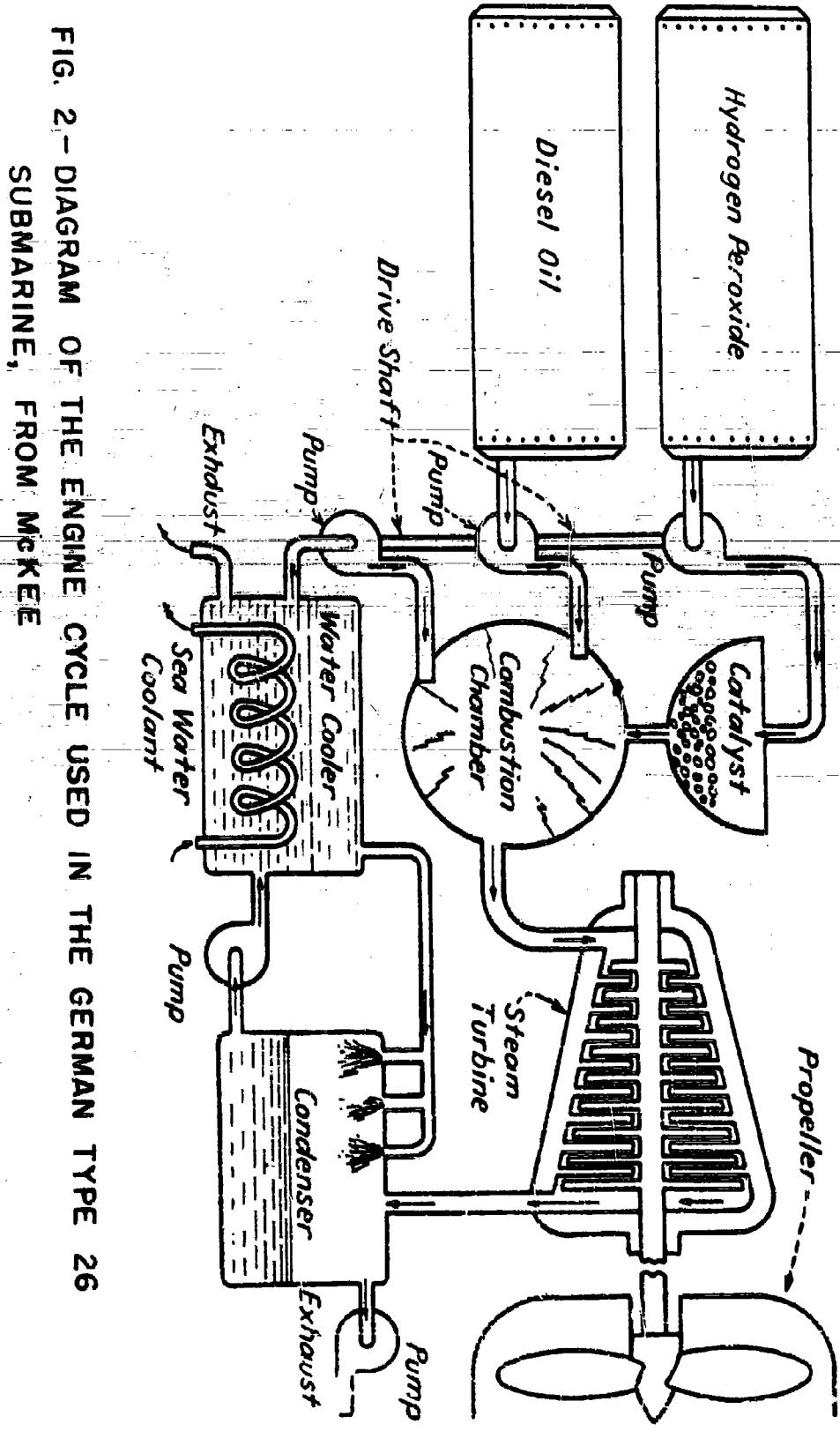


FIG. 2 - DIAGRAM OF THE ENGINE CYCLE USED IN THE GERMAN TYPE 26  
SUBMARINE, FROM MCKEE

tional torpedoes used by the various belligerents were powered either by electric batteries and motor or else by combustion of a fuel (e.g., alcohol, kerosene, decalin) in air supplied from compressed-air tanks. The hot combustion gases were then expanded through either a reciprocating engine or turbine which drove the propellers. Replacing the air with oxygen or hydrogen peroxide reduces the weight for a specified performance, or permits the attainment of higher speeds, ranges, or increased war-head size. Liquid oxygen was used in the Japanese type 93 torpedo but it introduces many problems of storage, maintenance and hazard.

A variety of German torpedoes were developed to use 80% hydrogen peroxide as the oxidant with decalin as the fuel. Combustion was initiated by injecting into the combustion chamber (in the first few seconds) an 80% aqueous solution of hydrazine hydrate, containing dissolved potassium copper cyanide or other copper compounds as a catalyst. This fuel spontaneously inflames with concentrated hydrogen peroxide. An additional advantage of the peroxide-driven torpedoes over those using air was that the combustion gases were readily soluble in water and therefore the torpedo could be made essentially wakeless. Considerable detail concerning the various German peroxide torpedoes is given in a report by Coleman and Kilpatrick (83). Mechanical details and performance data of two different German torpedoes using hydrogen peroxide have also been published by Maxfield (87) and compared with those of other torpedoes. It is reported that about 1000 peroxide-driven torpedoes of various types were manufactured in Germany during World War II.

#### Use in Rocket Propulsion

The relatively high cost of concentrated hydrogen peroxide relative to liquid oxygen or nitric acid limits its applications as the oxidizer in rocket propulsion, particularly for large rockets. Its largest scale use was in the Me163 interceptor airplane developed in Germany during World War II, which was the first rocket-propelled piloted aircraft ever flown.

In the first stages of development, a simple power plant utilizing the decomposition of concentrated hydrogen peroxide alone was used. However, the specific impulse of this system is quite low and it was replaced by a bi-propellant "hot" unit using a fuel consisting of a mixture of 30% hydrazine hydrate plus dissolved catalyst (potassium copper cyanide), 57% methyl alcohol and 13% water. This fuel was self-igniting with hydrogen peroxide. Methyl alcohol was used in the fuel mixture to extend the supplies of hydrazine hydrate and water was added to reduce the combustion temperature. The aircraft weighed 9020 pounds when fully fueled and the rocket motors could produce a 3300-pound thrust, which enabled it to climb to 30,000 feet in about two minutes. Even though 49% of the take-off weight of the airplane was propellant, its operational radius was extremely limited, and it had a normal endurance of only 10 - 20 minutes at the most. The fuel supply was sufficient for only 4 minutes at the maximum rate of consumption. More details including performance data on the Me163 aircraft are given by Walter (79) and by Zucrow (88), who also cites the performance characteristics of various liquid propellant systems in rocket motors.

Hydrogen peroxide was also used with fuel containing hydrazine hydrate in some German assisted-take-off units which provided additional thrust during take-off of aircraft and then were dropped. A typical unit was the HWK R1-209 used with the Heinkel He-111 and Junkers Ju-88. The motor weighed 500 pounds empty; it carried 486 pounds of peroxide solution, 61 pounds of fuel and produced a thrust of 3300 pounds for 30 seconds. However, take-off units based on decomposition of peroxide alone (with aqueous sodium permanganate or calcium permanganate solution as the catalyst) were also used, particularly for smaller aircraft where their greater simplicity more than compensated for the lower specific impulse obtained. As examples, the Focke-Wolf ATO FW-56 developed 650-pound thrust for 30 seconds; Henkel units He-111 and He-126 developed a maximum of 2200- and 1100-pound thrust. More details are given by Walter (79).

A monopropellant or "cold" take-off unit, called "Sprite," has been recently announced by the DeHavilland Engine Co., for general application to jet aircraft, civil or military. Two units would be used on take-off. Each holds 39 gallons of 80% peroxide, 2½ gallons of permanganate catalyst solution, weighs 925 pounds, and develops 5000 pounds thrust for 9 seconds. Complete design details are given (89). Solid propellant take-off units are simpler in construction than liquid propellant units and are frequently preferred today.

Collins (90) has made a detailed study of the performance of a small rocket motor (about 10 pounds thrust) using 90% hydrogen peroxide and two different self-igniting fuels, (1) an 85% aqueous solution of hydrazine hydrate containing iron and copper salts as catalysts, and (2) methyl alcohol containing 200 grams/liter of ferrous  $\beta$ -naphthalene sulfonate trihydrate. It was found that the performance obtained in such a small rocket motor can closely approximate that commonly observed in a large-scale motor which provides an approximately equal residence time for the reactants. The experimental results are compared with theoretical predictions and the problem of how to allow for heat loss in making such a comparison is considered in particular. Considerable information is also given on the performance of various types of injectors.

A very readable book which recounts the development of rocket propulsion has been prepared by Willy Ley (91). For a more technical analysis of rocket and jet propulsion, see the books by Zucrow (92) or Sutton (93). The principles of rocket propulsion and design and performance of liquid propellant rockets are also presented by Seifert, Mills and Summerfield (94) and by Diplock, Loftus and Grimston (95).

#### Use in an Auxiliary Power Source

The continuous, complete decomposition of hydrogen peroxide produces a super-heated steam-oxygen mixture at a constant temperature, fixed by the peroxide concentration used,

and can thereby provide a simple, reliable and compact auxiliary energy source. It was thus used in the German V-2 rocket to power the fuel pumps which forced the main propellants, liquid oxygen and 75% ethyl alcohol-25% water, into the combustion chamber. In the V-2 rocket the stream of peroxide was decomposed in a decomposition chamber by injecting continuously an aqueous solution of sodium or calcium permanganate, although a mechanical system using flow through a bed packed with active catalyst would be simpler. A particular advantage of hydrogen peroxide in this application is that the temperature of the decomposition gases is sufficiently low that no diluent need be added before they enter the turbine.

#### Use in Catapult Launching

The German V-1 flying bomb, which was a miniature robot aircraft powered by an intermittent (pulse) jet, was launched from the ground by a piston-type catapult powered by concentrated hydrogen peroxide decomposed with sodium or calcium permanganate solution. Each launching required about 220 pounds of 80% hydrogen peroxide solution plus 11 pounds of calcium permanganate solution.

The two fluids were sprayed into the gun breeching from blow cases pressurized by air bottles; the peroxide decomposition produced an internal pressure of 800 - 1000 psi. A launching speed of about 250 miles per hour was attained with a 150 ft. guntube, corresponding to an average acceleration of about 15 times gravity, which meant that reaction must be essentially completed within the launching period of 0.75 seconds. An ingenious mechanical device was used to connect the flying projectile above the guntube with the piston inside.

The characteristics of the German launcher have been described by Bellinger *et al.* (96) who also report studies of hydrogen peroxide decomposition by permanganates in thrust motors. These were carried out in a preliminary investigation by the U. S. Chemical Warfare Service of the use of liquid propellants for launching an American counterpart of the V-1 bomb.

In possible ordnance uses of liquid propellants, very high chamber pressures may be encountered. Barr and Wilson (97) have published results of calculations of the thermodynamic properties of the reaction products of 100% hydrogen peroxide and 100% hydrazine at pressures of 10,000 to 185,000 pounds per square inch. The data include final equilibrium temperatures, densities and gas compositions for reaction under either constant pressure or constant volume conditions.

#### Hydrogen Peroxide as an Explosive

As discussed in Chapter 4, certain mixtures or solutions of organic substances in concentrated hydrogen peroxide form very-sensitive and powerful explosives. For commercial use, however, it is necessary that an explosive have a very low sensitivity. Certain mixtures of glycerol, hydrogen peroxide and water have been found to be insensitive to mechanical impact such as rifle fire, but detonatable by a blasting cap (98). The fact that the two liquids are each non-explosive by themselves offers a method for safe transportation and storage, since the explosive mixture need be formed only at the site and then only shortly before it is to be used. However, there is no report of these mixtures having been actually used commercially. The reaction of hydrogen peroxide with certain substances such as powdered aluminum and carbon has been suggested (99) as the basis for preparation of delayed-action fuses, although the reactions appear difficult to regulate.

#### USE OF GAS FORMED ON DECOMPOSITION OF HYDROGEN PEROXIDE

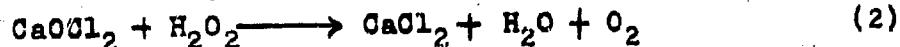
The fact that hydrogen peroxide releases a gas on decomposition or in certain reactions is the basis for its use in the manufacture of porous products. Thus it has been used to manufacture porous concrete building blocks, in foam rubber manufacture, and it has also been considered as a dough-leavening agent. Hydrogen peroxide is a convenient source of pure oxygen. The gas formed on decomposition may also find use as a flotation agent, as in the recovery of pulp from mill waste.

### Use in Porous Concrete

For many building applications it is desirable to use a low density building block or construction material in order to save weight or for its insulating value. In the United States expanded perlite or other low density aggregate is frequently incorporated in a concrete mixture for this purpose. Considerable experimental work was carried out in Germany before and during World War II on the use of hydrogen peroxide to produce a porous product from cement mixtures. Procedures varied depending upon the nature of the aggregate and desired properties of the product. A typical mix contained the following ingredients added in the order given:

- (a) 600 kilograms of fine sand
- (b) 300 " " cement
- (c) water
- (d) 3.5 liters of 40% hydrogen peroxide
- (e) Calcium hypochlorite equivalent to the hydrogen peroxide, as expressed by the reaction below.

The use of catalysts to decompose the hydrogen peroxide was found to be unsatisfactory. Calcium hypochlorite is not a catalyst but reacts as follows:



The building blocks produced were reported to have a specific gravity of about 1, a crushing strength of about 25 - 30 kilograms/sq cm and 2 - 3 times the insulating value of ordinary building blocks. This product was used in substantial quantities by the German Army as a building material. Doubling the amount of hydrogen peroxide used and adding about 0.7% of shredded cellulose from wood pulp, based on the dry weight of cement plus sand, produced blocks with specific gravity of about 0.5 and crushing strength of 20 kilograms/sq cm. Porous gypsum block was also made, using decomposition catalysts with hydrogen peroxide, having a specific gravity of about 0.3 and a crushing strength of about 4 kilograms/sq cm. Porous concrete made with hydrogen peroxide

does not adhere as well as ordinary concrete to steel reinforcing rod, since the peroxide is decomposed by the metal, forming a gas film between the rod and the concrete. However, one advantage of the use of hydrogen peroxide here over many other chemical agents is the fact that the gas can be produced without heating.

#### Foam Rubber

Foam rubber products are made by incorporating various ingredients in natural or synthetic latex, among which is a chemical such as hydrogen peroxide which will liberate gas. The actual techniques used have not been publicized by the manufacturers but it is known that the quality of the final product is greatly dependent upon such factors as sequence and timing of the additions. In one process, after addition of the hydrogen peroxide, the latex batter is allowed to expand to the desired degree in the mold, which is then quick frozen to preserve the shape and cellular structure. This is followed by curing, and then washing.

A recent Swiss patent (100) quotes the following formulation: to 1 liter of a latex mixture containing 100 parts latex, 3 sulfur, 8 zinc oxide, 1.5 accelerator and 1 part pigment, is added 10 milliliters of 30% hydrogen peroxide. The mixture is stirred until it reaches a volume of 5 liters, whereupon 150 ml of 15% calcium casein and 20 ml of 20% ammonium chloride are added. The foam, which is claimed to be stable for 3 - 5 hours, is then vulcanized at 95° C. Other formulations are also given. The final total volume is generally determined by the quantity of hydrogen peroxide added, and soap may be added to control bubble size.

#### Use of Hydrogen Peroxide in the Leavening of Dough

Several patents have been issued on the use of hydrogen peroxide or peroxy compounds as a dough-leavening agent (101). Hydrogen peroxide equivalent to 0.5 - 2.0% of the weight of the dry flour is incorporated into the dough, and it is allowed to

stand until most of the peroxide has disappeared, before it is baked. The remainder then becomes destroyed, during the baking operation, by the catalase present. Since catalase itself is destroyed by elevated temperatures, it is important that the baking operations be so adjusted that all the hydrogen peroxide has disappeared by the time that the catalase-destroying temperatures are reached. A comparison of bread leavened with yeast and with hydrogen peroxide was made by Bailey and Le-Clerc (102) who carefully analyzed crust and crumb for ash, fat, reducing sugar, total sugar, water-soluble solids, etc. Few significant differences were found, except that the taste of the peroxide bread was reported to be inferior to that of yeast bread. It has also been objected that the texture of bread or cake leavened with hydrogen peroxide is too fine and regular; the strength of the product is low and in the mouth it produces a drying sensation because of the enormous absorptive power endowed by the fine texture. Solid peroxy compounds such as calcium peroxide and urea peroxide have also been proposed as baking powder ingredients (103).

#### Hydrogen Peroxide as a Source of Oxygen

The use of hydrogen peroxide specifically to generate oxygen has not been exploited to a great degree outside the laboratory. It has been proposed for replenishment of the atmosphere, as within a submarine, and has been used to keep fingerling fish during shipment. Consideration of concentrated hydrogen peroxide as an oxygen source for welding and other uses in remote places may well be warranted, since 90% hydrogen peroxide offers a weight saving of more than 50% over conventional cylinders of oxygen; return of empty containers is even more economical. Where larger quantities of oxygen are required, a liquid oxygen plant becomes in turn more attractive.

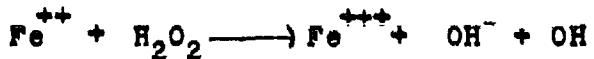
Dilute hydrogen peroxide solutions are a convenient source of small quantities of oxygen, such as might be desired in laboratory work or in lecture demonstrations. A convenient procedure is to run the hydrogen peroxide solution into a con-

tainer or an apparatus operating on the principle of the Kipp Generator and containing a solid catalyst such as manganese dioxide.

### HYDROGEN PEROXIDE AS A SOURCE OF FREE RADICALS

#### Polymerization Catalyst

The polymerization of most unsaturated compounds, such as styrene, vinyl acetate, methyl methacrylate, etc., can be accelerated by addition of hydrogen peroxide or other peroxy compounds (104). The effect is due to the free radicals produced on decomposition of the peroxide, which are known to initiate polymerization chains. Varying the concentration of peroxide used and other experimental conditions provides considerable control over the average molecular weight and other properties of the product. The addition of small amounts of polyvalent metal catalysts, such as iron, greatly increases the production rate of radicals by peroxide decomposition and thereby makes it possible to achieve substantial polymerization rates at much lower temperatures. By this means, polymers of superior physical properties can be produced, such as "cold rubber" in the synthetic rubber field. The initial reactions occurring are shown in the equations below:



Any one of a number of peroxy compounds may be chosen for use as a polymerization catalyst. For example, potassium peroxydisulfate was used during the 1940's in the United States for co-polymerizing butadiene and styrene; a number of organic peroxides such as benzoyl peroxide and cumene hydroperoxide have found various applications.

Depolymerization of polymers such as cellulose, starch, rubber, etc., is also accelerated by peroxides, but the effect is probably due to the oxidation and subsequent breakage of bonds

rather than to the formation of free radicals as such.

Other organic reactions which proceed by a free radical mechanism may be catalyzed by peroxides. Examples include the addition of polyhalogenated hydrocarbons such as bromoform and the addition of phosphorus trichloride to double bonds of an olefin (105).

#### EFFECTS OF HYDROGEN PEROXIDE ON BIOLOGICAL PROCESSES

##### Use of Hydrogen Peroxide in Medicine

Hydrogen peroxide was first introduced into medical practice by Richardson in 1856. Following Richardson's ardent recommendations, many treatments involving the use of hydrogen peroxide were developed and these are reviewed by Richardson (106) and Wallian (107). Those treatments which were developed for specific diseases were chiefly symptomatic and few would be recognized today. Similarly, the introduction of hydrogen peroxide as an antiseptic or disinfectant occurred at a period before the necessity for asepsis in medical and surgical procedures was commonly recognized and based upon scientific principles. These facts reduce the extensive earlier medical literature to little more than historical interest.

The area of usefulness of hydrogen peroxide as an antiseptic and disinfecting\* agent and as a treatment for certain diseases may now be outlined more certainly. These medicinal uses of hydrogen peroxide do not account for a large proportion of the hydrogen peroxide marketed, but the use as a household antiseptic is widespread. Although antiseptic agents also possessing bactericidal power have displaced some of the favor formerly accorded hydrogen peroxide, public familiarity with hydrogen peroxide is

\* The terms antiseptic and disinfectant, as well as the similar terms bactericide, bacteriostat, germicide, virucide and sterilizing agent, are often used synonymously. Strictly, antiseptic is taken to mean that which inhibits the growth of micro-organisms without necessarily destroying them, as distinguished from a disinfectant, that which frees completely from infection, killing micro-organisms and rendering viruses inactive.

largely confined to the use as antiseptic and as a hair bleach. Various other peroxy compounds have also come into use for medical purposes. For example, urea hydroperoxide in glycerine has been extensively studied and appears to have considerable effectiveness. Inorganic peroxides such as zinc and calcium peroxides have been incorporated into cosmetics and tooth paste because of their antiseptic action. Hydrogen peroxide also has been incorporated in pastes, tablets, ointments, etc.

Many detailed studies have been made of the bactericidal action of hydrogen peroxide and peroxy compounds against various microorganisms (108) and its efficacy has been compared (109) with such other bactericides as the mercuric compounds, iodine, phenols, ethyl alcohol and others. However, their reported relative effectivenesses vary greatly with the method chosen for comparison, type of organism studied, concentration of the agent, and time of contact.

The in vitro testing of an antiseptic or disinfectant is, as it were, the measurement of a chemical reaction rate, with concentration, temperature, and, to a limited extent, solvent or growth medium as the variables. When it is attempted to extrapolate these results to the probable action in tissue fluids there enters a host of other variables which are difficult or impossible to duplicate simultaneously in in vitro tests. In addition there must be considered, especially in the treatment of wounds or the surface of the skin and mucous membranes, the rate of transport of the antiseptic to the affected area and its time of residence there in the presence of forces for destruction and dilution. Such physical rate processes may play a determining role in the effectiveness of an antiseptic. These considerations are discussed in the monograph by McCulloch (110) and, for hydrogen peroxide in particular, by Brown (111). The results of the studies cannot be detailed here; in general hydrogen peroxide-glycerol solutions seem to be more effective against gram positive than against gram negative organisms, although bacteriostatic effects are shown against both, and hydrogen peroxide can be classed as

a non-specific bactericide. Higher hydrogen peroxide concentrations and/or longer contact time are needed to destroy spore-forming bacteria such as B. subtilis than are needed for coliforms such as E. coli. A particular advantage to the use of hydrogen peroxide as a disinfectant is that it produces relatively little inhibition of phagocytosis (activity of certain blood and other cells in destroying waste, harmful bacteria, etc.). In general, tests in vitro show that peroxide concentrations of the order of 0.001% - 0.1% at room temperature inhibit growth while concentrations of very roughly 0.1% or higher destroy the organisms. Such concentrations are also capable of rendering solutions intended for injection pyrogen-free (112). This subject is also discussed in Biological Processes in Chapter 2.

The advantages and disadvantages of hydrogen peroxide as an antiseptic may be summed up as follows:

<u>Advantages</u>	<u>Disadvantages</u>
not unduly specific	slow in action
low tissue toxicity	relatively unstable in storage
non-allergenic	high surface tension
innocuous products of decomposition	inactivated by tissues
non-staining	
soluble in tissue fluids	
exerts cleansing action	
relatively inexpensive	
relatively painless	

The disadvantages mentioned are overcome to a large degree by replacing water with anhydrous glycerol as the solvent. Such a preparation, to which hydrogen peroxide is added as urea hydroperoxide and containing oxine as a stabilizer, has been developed by Brown, Gorin and Abramson (113). The viscous glycerol vehicle prolongs the action of the hydrogen peroxide by preventing evaporation, clinging to the point of application, and providing a reservoir of peroxide which continually diffuses

to the surface to be treated rather than being quickly decomposed by surrounding tissues. The hygroscopic glycerol also aids by drawing tissue fluid to the site of action. Brown (114) has found a high degree of tissue tolerance and lack of sensitivity to this preparation. Studies (115) of this and other hydrogen peroxide antiseptic preparations indicate that acceptable stability can be maintained for long periods.

The ultimate mechanism whereby hydrogen peroxide exerts antiseptic or disinfectant action is not understood. It is known (116) that hydrogen peroxide is a normal metabolite of bacterial growth; thus increase of hydrogen peroxide concentration in the bacterial growth medium acts as an inhibitory concentration of waste, retarding or stopping growth. Similarly, the release of oxygen may inhibit the growth of an anaerobe. The synergistic action with phagocytes (117) already mentioned may also play a part in the action. On the other hand, naturally-occurring substances inhibit action of hydrogen peroxide as by the decomposition with catalase (118) or the protection afforded by pyruvate (119). The addition of certain salts to hydrogen peroxide, i.e., those of iron, copper, chromium (promoted with manganese or cobalt), and molybdenum, has been shown (120) to increase the disinfectant power markedly, suggesting that the formation of free radicals may play a part. This is similar to the power of hydrogen peroxide, alone and in Fenton's reagent, to produce mutations (121) in bacteria as does radiation.

Hydrogen peroxide has also been proposed as an intermediate in antiseptic and detoxification mechanisms of medical interest. The action of sulfanilamide has in part been ascribed (122) to the depression or neutralization of catalase activity which allows hydrogen peroxide derived from bacterial metabolism to increase to an inhibitory concentration. Saliva has been shown to have some antiseptic action and it has been stated (123) that this is due to the presence of hydrogen peroxide. The action of phenols on bacteria has been shown (124) to be heightened by the presence of peroxidase and hydrogen peroxide, although it is

not certain that this effect is of any significance in the action of unpromoted phenol. Hydrogen peroxide has also been assigned (125) an intermediate role in the detoxification action of ascorbic acid on cyclic compounds. The formation of hydrogen peroxide by bacteria and by enzyme processes is discussed in Chapter 2.

References may be given to recent descriptions of the use of hydrogen peroxide in the treatment of specific diseases or afflictions. Good results have been obtained in treating chronic ear infections (126), a number of inflammatory or bacterial and fungus infections of the skin and mucous membranes (127), cyanide poisoning (128), chronic empyema and lung infections (129), reduction or prevention of skin lesions caused by friction of rough paper (130), anorectal surgery (131), warts, small burns and Lewisite burns (132). Several applications to veterinary medicine have been described by Emmerson (133); use as a vermifuge or anthelmintic (134) and in the treatment for warble flies (135) is also successful. The use in treating gas gangrene (136), influenzal pneumonia (137) and stomach ulcers (138) may be said to be controversial or unsuccessful, and treatment of hypoxia, carbon monoxide poisoning, hemorrhage and shock with hydrogen peroxide has been found of no value in animal experiments (139).

#### Seed Treatments

A substantial number of reports have been published of the use of hydrogen peroxide or peroxy compounds for treating seeds. The most common purpose is to disinfect the seeds and improve the germination. It is relatively easy to determine the effectiveness of a disinfecting treatment, but it is far from clear whether the improved germination obtained in some cases is due to immobilization of microorganisms which would otherwise interfere with germination, or rather to the specific effect on the germination power of the seed. Too severe disinfection treatments may strongly reduce germination. The sterilizing effect of hydrogen peroxide varies with the character of the seed coat and the type of microorganism. Kissner and Portheim (140)

found that flower, legume and cereal seeds could be partly or completely sterilized with little impairment of germination, by use of solutions of hydrogen peroxide of 15 or 30 wt. %.

Rough seeds, those covered by glumes (husks), and those occurring in balls were more difficult or impossible to sterilize. Those treatments which favored penetration of the peroxide solution into the seed decreased germination. Pichler (141) reported that treatment of wheat and barley with hydrogen peroxide solutions of up to 3 wt. % failed to control wheat bunt (Tilletia caries) or covered smut of barley (Ustilago hordei) and treatment of oats with solutions of 4 - 5 wt. % failed to control the loose smut of oats (U. Avenae). Olgyay (142) found that solutions of about 20% hydrogen peroxide were required to disinfect grain infested with smut (in 5 minutes contact time), but germination was slightly decreased.

There are several reports in the literature of hydrogen peroxide treatments being only slightly or not at all effective in overcoming seed infections, but in each case it appears that too low peroxide concentrations were used (i.e., 5 wt. % or less). There are also some indications that peroxyacetic acid may be an effective agent for seed treatments.

Soaking seeds in dilute peroxide solutions (e.g., 0.01 to 1.5 wt. %) for periods of 1 day or so or until germination begins, improves the percentage germination and the rapidity or intensity of germination of a number of seeds. Improved effects have been reported for wheat (143), flower and legume seeds (144) and tomato seeds (145). There have been a number of studies on barley which show improved germination characteristics, this being of particular interest to breweries. Typical hydrogen peroxide concentrations are 0.01 - 0.5% in the steep liquor and optimum temperature of 20°C (146). The fact that water is the only residue of the treatment makes it of particular interest here. Most of the work done before 1939 on use of hydrogen peroxide in treating barley for malting purposes has been summarized by Raux (147). A more recent study by Bawden (148) indicated

that small concentrations of hydrogen peroxide in the steep were much more effective in stimulating germination than were plant-hormones. The use of peroxygen chemicals in seed treatments has been discussed in a recent industrial bulletin which includes 17 literature references on the subject (149).

The application of hydrogen peroxide or certain other oxidizing agents to the soil is reported to improve the yields of corn and soybeans (150) or the growth of seedlings (151). The reason for the effect is uncertain. It has been suggested (151) that the oxidizing agent hastens decomposition of the organic material in the soil; alternately it may directly affect the seed as indicated above. Another possibility is that reaction of hydrogen peroxide with inorganic soil components may leave them in more readily assimilable form. Mechanical action, due to the oxygen evolution on decomposition, may also improve the soil, leaving it more porous. This action becomes more pronounced as the concentration of hydrogen peroxide is raised; when 90% hydrogen peroxide is poured on earth the decomposition is quite vigorous and after decomposition leaves the surface layer of the soil powdery and increased in apparent volume and, even with wet soil, dry as a result of the heat evolved.

#### Preparation and Preservation of Food and Drink

It has been attempted or proposed to use hydrogen peroxide in the preparation or preservation of a number of foodstuffs and potables, although only a few of these uses have received common acceptance. Procedures have been described for the preservation, by the addition of small proportions of hydrogen peroxide, of milk and other dairy products (discussed below), fish (152) (through incorporation of hydrogen peroxide in ice used for packing), canned bouillon (153), eggs (154), sake, vinegar, ketchup, coffee syrup, bean curd, vermicelli (155), cocoa syrup (156), lecithin, gelatin, pickles and starch.

The purification of water by treatment with hydrogen peroxide has been considered (157). This subject is reviewed by Reichel (158), who concluded on the basis of his own experi-

ments that effective disinfection of water requires addition of proportions of hydrogen peroxide as large as 5 wt. % if disinfection is to be complete within a practical time period. At this concentration the taste of the residual hydrogen peroxide is evident and it must be destroyed by the addition of a non-objectionable catalyst. If longer periods of time for treatment are feasible, the disinfection of water may be accomplished with less hydrogen peroxide, e.g., 0.5% suffices in a 24-hour period. Hydrogen peroxide may also be used to destroy the taste of chlorine in water treated by conventional methods. Sterilization of containers, pipes, filters, etc., used in the food industry is often accomplished with hydrogen peroxide.

The bactericidal and fungicidal action of hydrogen peroxide has been applied to food in the proposed improvement of moldy grain (159), and a similar procedure is applied in the process of preventing the deterioration of freshly picked fruits and vegetables (160) (a parallel, or perhaps identical in basic mechanism, procedure for the spraying of tomatoes with peroxyacetic acid has been extensively developed (161)). Undesired fermentation of grape must in storage is halted by the addition of hydrogen peroxide (162).

Other proposals for the treatment of foods with hydrogen peroxide, although not concerned with preservative action, are the uses as the rising agent in baking, described previously, in a process for the improvement of wine and Cognac (163) (maturing is hastened, presumably through the conversion of fusel oil to aldehydes by reaction with hydrogen peroxide), in the recovery of culture media (164), in the removal of bitter principles from yeast (165), to stabilize lecithin (166), in a process for the enhancement of the flavor of edible oils (167), in the modification of edible starches and gums (168), in the improvement of the taste of coffee extracts (169), to bleach monosodium glutamate, in bleaching tripe, gelatin and egg yolk, and in the bleaching of nuts and dried fruits to improve their appearance. Large quantities of hydrogen peroxide are used indirectly in the food industry through the widespread use of benzoyl peroxide for

the bleaching of flour. Flour bleaching (oxidation of xanthophyll) with benzoyl peroxide is rapid and uniform, but there is no concurrent maturing effect, i.e., improvement of baking quality.

Where the proposed action of hydrogen peroxide is that of a preservative, two mechanisms of action may be distinguished: the destruction of enzymes which are responsible for deteriorating changes in composition, and the elimination or inhibition of the growth of pathogenic or deteriorating organisms. It is generally intended that the dosage be so regulated that the mutual destruction of the added hydrogen peroxide and the particular substrate in question act to eliminate both, leaving no residual hydrogen peroxide. Since the sensitivity, composition, and history of handling and treatment may vary so widely, even for different samples of the same food or drink, it is difficult to reach a decision regarding the possible effectiveness, alteration of taste, change in nutrient value, or physiological consequences to be expected in any given case from treatment with hydrogen peroxide. The evaluation is further complicated by the fact that the formation of hydrogen peroxide through autoxidation reactions in food has been put forward as a cause of deterioration. It is clear that the use of hydrogen peroxide, or any preservative for that matter, cannot be condoned as a substitute for sanitary handling or adequate processing of food, as in the proposed use for the upgrading of spoiled meat. At the other extreme, however, it is not clear whether the employment of hydrogen peroxide as a preservative offers a desirable and economical procedure for the food and beverage industry. The proposed use of hydrogen peroxide as a preservative for milk has received the most widespread consideration. The following, more detailed, description of this potentially useful and seriously advocated use of hydrogen peroxide may serve as a typical example of the problems to be met in the treatment of food or drink.

The early history of the investigation of hydrogen peroxide as a preservative for milk has been reviewed by Amberg (170) and by Anselmi (171); the procedure was first suggested by Baldy

in 1881, and was used in France and Germany (172) during the war of 1914, but later banned. Preservation of milk in any other fashion than by pasteurization and refrigeration is now prohibited in many places, but the use of hydrogen peroxide for this purpose was revived in Italy during the war of 1939, and much of the recent research in this field has been that of Italian workers.

The work of Chick (173) (1901) has been widely quoted and taken as a point of departure in much subsequent work. Chick stated that milk could be sterilized completely by the addition of two parts of hydrogen peroxide, expressed on a 100% basis, per thousand parts of milk. Upon addition of this proportion of hydrogen peroxide there was an initial decomposition after which the concentration of hydrogen peroxide remained constant for a long time. Since Chick claimed to be able to detect the alteration in taste of the milk due to the presence of one part of hydrogen peroxide in 10,000, she did not believe the procedure to be a practical one; a treatment sufficient for sterilization would make the milk unpalatable.

Rosam (174) found two parts per thousand inadequate and suggested combining a heat treatment with hydrogen peroxide addition. This procedure was elaborated upon by Budde (175) who developed in Denmark a commercial process for the addition of 0.9 g/l of hydrogen peroxide, expressed on a 100% basis, followed by heating at 50°C for several hours; if hydrogen peroxide then remained in the milk it was destroyed by the addition of yeast. Later workers disputed the quantity of hydrogen peroxide necessary, various proportions up to 1% being recommended. It was pointed out that the effectiveness varied with different samples, that the temperature of treatment and storage, the pH, and the type of microorganisms present in the milk all exerted an influence on the quantity necessary to sterilize the milk and to affect the taste. It was recognized that as long as hydrogen peroxide was present coagulation would not occur, but opinion was divided on the question of whether the presence of sufficient hydrogen peroxide to suppress souring was likewise sufficient to kill

pathogenic organisms. Several accounts of prolonged feeding of hydrogen peroxide-treated milk were given, all with no untoward physiological effects.

More recent investigations have improved the understanding of the effects of the addition of hydrogen peroxide to milk. Furthermore, the general availability of electrolytically-produced 30% hydrogen peroxide has eliminated the earlier objections to "watering" of the milk and introduction of undesirable metallic impurities by the use of 3% hydrogen peroxide from the barium peroxide process.

There is now general agreement that hydrogen peroxide added to raw milk immediately after milking, in the proportion of about 0.1% by weight (100% basis), will reduce the content of pathogenic organisms to an acceptably low level and will prevent souring during storage at room temperature for several days. This conclusion is supported by the work of Morandi (176) (also reported by Dahlen and Grossley (177)). If the milk is kept at a lower temperature, a smaller proportion of hydrogen peroxide suffices to preserve it, as shown by Satta, Morandi and Moggi (178), or conversely, if the proportion of hydrogen peroxide is not reduced, the milk will keep longer, e.g., 32 - 40 days at 5°C according to Romani (179). By combining pasteurization with hydrogen peroxide treatment, smaller proportions of hydrogen peroxide are also effective in postponing souring; Sanders and Sager (180) found 0.1% by weight sufficient to prevent the curdling of pasteurized milk containing 2.5% raw milk for 10 to 21 days in testing the use of hydrogen peroxide to preserve milk samples before analysis.

The diminution of the bacterial count in milk brought about by the addition of 0.1% hydrogen peroxide was found to be about 95% by Morandi (176). Peragallo (quoted in reference 177), studying milk artificially contaminated with b. coli, b. typhicus, brucella melitensis, brucella abortus, and cattle tubercle bacillus, found the action of 0.1% hydrogen peroxide added immediately after milking to be bactericidal to all but tubercle bacillus in measure-

ments over periods of 12 to 48 hours. If some time elapsed after milking, before the additions of hydrogen peroxide, its action was only bacteriostatic, allowing significant regeneration within the time periods studied. These findings are substantiated by Heinemann (181), Rosati (182), Gentili and Romagnoli (183) and Monaci (184).

The effects of the addition of hydrogen peroxide upon the physical and chemical properties and enzyme and vitamin content of milk are shown in Table 5. Studies of the rate of increase of acidity after addition of varying amounts of hydrogen peroxide and under different conditions of storage and contamination have also been made by Anselmi (171) and Caserio (quoted in reference 177); these bear out the earlier assertion that the milk does not sour appreciably during the period over which the milk is preserved by the presence of hydrogen peroxide.

Anselmi (171) presents qualitative observations on the increased tendency to froth and form a film of agglomerated material on the walls of containers.

The effect of hydrogen peroxide on the organoleptic properties of milk is pronounced but not lasting. Nearly all who have worked on this subject agree that both smell and taste are too seriously impaired when effective concentrations of hydrogen peroxide are used, if the residual hydrogen peroxide is not decomposed before consumption of the milk. It is for this reason that the various proposals for the use of hydrogen peroxide have included a heat treatment, catalyst addition, or a holding period, or have recommended that its use be confined to preservation during the time between milking and pasteurization. This may not be a disadvantage, however, since several recent patents (192) stress the fact that complete sterilization is possible with hydrogen peroxide treatment followed by heating, whereas in order to sterilize by pasteurization alone, milk must be heated to such high temperatures or for such prolonged periods that the taste and physical properties are affected adversely.

Two effects of hydrogen peroxide upon the taste of

TABLE 5

## THE EFFECTS OF THE ADDITION OF HYDROGEN PEROXIDE UPON PHYSICAL AND CHEMICAL PROPERTIES AND ENZYME AND VITAMIN CONTENT OF MILK

Property or Substance	Approx. Propor-tion of $H_2O_2$	Effect	Reference
Density	0.1 wt. %	none	(177)
Freezing Point		"	"
Serum Refractivity		"	"
Fat Content		"	(177) (185)
Total Nitrogen Content	0.3 wt. %	"	"
Amino Acid Content		"	(186)
Casein	0.1 wt. %	decreased	(185)
Albumin		increased	(177) (185)
Milk Sugar		none	(177)
Polenske No.		"	"
Reichert-Meissl-Wollny No.		"	"
Refractive Value of Fat		"	"
Size, Structure of Fat Globules		"	"
Creaming Velocity		"	"
pH		decreased	"
pH		none	(185)
Oxidation-Reduction Potential		changed	(187) (188)
Action Upon, by Rennet	0.1 wt. %	inhibited	(177)
Catalase Content		decreased	(177) (189)
		or destroyed	"
Reductase Content		"	"
Peroxidase Content		"	(189)
Amylase Content		none	"
Lipase Content		"	"
Tryptase Content		"	"
Phosphatase Content		"	"
Vitamin A	0.1 wt. %	decreased	(180)
Vitamin B		"	(178) (185)
Vitamin C		decreased	(177) (178)
Vitamin D	0.1 wt. %	or destroyed	(190) (191)
		none	(178)

milk can be distinguished. The first is simply that of imparting, at sufficient concentration, a taste characteristic of hydrogen peroxide, which has been described as "metallic." The second effect is more complicated: hydrogen peroxide enters into and alters the course of the reactions which may normally bring about a change in the flavor of milk. On storage, untreated milk may gradually develop an oxidized or "tallowy" flavor, stated by Krukovsky and Guthrie (193) to be due to the oxidation of unsaturated fatty acids, primarily oleic acid, in the lipid fraction of milk. The phospholipid present in the membrane of the fat globules is thought to be most susceptible to oxidation (194), although Pont (195) doubts that the phospholipid is the source of the flavor.

Greenbank (188) found that the effect of the addition of hydrogen peroxide upon the development of an oxidized flavor varied from promotion to inhibition as the proportion of hydrogen peroxide was varied from 0.001 to 0.016 wt. % and believed that the change in oxidation-reduction potential accounted for the inhibiting effect. Krukovsky and Guthrie (193) placed the limit of the inhibiting effect lower, at somewhat less than 0.001 wt. % and observed the development of the oxidized flavor after varying times in milk containing less than this proportion of hydrogen peroxide. This action is explained by Krukovsky and Guthrie to be due to the oxidation of ascorbic acid to dehydroascorbic acid. They believe the lipid oxidation to be a coupled reaction dependent upon a certain equilibrium between ascorbic acid and dehydroascorbic acid and possibly catalytically initiated.

The rate of oxidation of ascorbic acid by hydrogen peroxide is inversely proportional to the hydrogen peroxide concentration, due to inactivation of the enzyme (believed by Krukovsky (196) to be peroxidase) catalyzing the oxidation. Thus at low concentrations of hydrogen peroxide, oxidation of ascorbic acid is rapid enough to set up a favorable ratio of ascorbic acid and dehydroascorbic acid for the lipid oxidation. At higher concentrations of hydrogen peroxide the rate of ascorbic acid oxidation is slower than the subsequent destruction of the labile and

sensitive dehydroascorbic acid, and a ratio of these favorable to lipid oxidation is not achieved before the complete oxidation of the ascorbic acid, thus inhibiting development of the oxidized flavor.

Other factors enter into this complicated process, which is reviewed by Chilson, Martin and Parrish (197) and by Greenbank (198). As a practical procedure for the deferment of oxidized flavor in frozen milk, Bell and Mucha (191) found addition of hydrogen peroxide to be effective but less satisfactory than fortification of the milk with ascorbic acid, which in increased proportion is preferentially oxidized, prolonging the time before lipid oxidation.

In conclusion, it appears that the use of hydrogen peroxide as a preservative for milk offers no advantages to recommend it as a replacement for pasteurization. Hydrogen peroxide treatment is apparently harmless from a physiological standpoint and does not seriously alter the nutrient value of milk, but since the treatment seems not amenable to close standardization and is powerful enough to conceal unsanitary handling it would be necessary to carry it out under competent technical supervision. As an emergency measure, in backward areas, or in military operations, preservation of milk with hydrogen peroxide may merit use; even in these cases it would seem preferable to combine the treatment with a heat treatment of some kind.

#### USE IN CHEMICAL SYNTHESIS

Hydrogen peroxide finds considerable application as the starting material for the preparation of most peroxy compounds and as an oxidant in organic synthesis.

The inorganic peroxy compounds are considered in Chapter 12 in which the methods of preparation are also indicated. The only compounds of this group which are not produced industrially via hydrogen peroxide are sodium peroxide, which is manufactured by burning sodium in air; barium peroxide, which is produced by peroxidation of barium oxide in air, and potassium and other peroxy-

disulfates, which are manufactured directly from ammonium peroxydisulfates or peroxydisulfuric acid formed as an intermediate in the electrolytic methods for manufacture of hydrogen peroxide. Sodium perborate may also be produced electrolytically from borax, but it is more commonly manufactured from a mixture of borax plus hydrogen peroxide and/or sodium peroxide.

Organic hydroperoxides may be produced directly by oxidation of hydrocarbons or other organic compounds with air, but a variety of by-products may be formed and industrial practice therefore usually favors the synthesis via hydrogen peroxide or another peroxy compound.

The various types of organic reactions involving hydrogen peroxide (or a peroxyacid) are described in Chapter 7. In addition to formation of organic peroxycompounds, these reactions include (1) reaction with an unsaturated bond to form an epoxy derivative ( $-R-\overset{O}{\diagdown}-R-$ ) or a glycol  $\overset{OH}{-}C=C-\overset{OH}{-}$ , (2) various oxidation reactions such as oxidation of a substituted naphthalene to the corresponding quinone and (3) ring splitting reactions such as conversion of phenol to muconic acid. Short reviews of some applications of hydrogen peroxide to organic synthesis are given by Johnson (199) and Friess (200).

A discussion of the industrial applications of organic peroxy compounds and of organic processes using peroxy compounds other than hydrogen peroxide is beyond the scope of this book. Some epoxy compounds are used directly, such as dieldrin, a recently developed insecticide. Other epoxy compounds are used for production of resins and surface active materials or as intermediates in organic synthesis. For example, in the synthesis of cortisone the 17-hydroxy group may be introduced by forming an epoxy intermediate followed by reduction to the hydroxy group. Examples of applications of organic hydroperoxides are their use as polymerization initiators and as Diesel fuel additives to increase the cetane number.

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## CHAPTER TWELVE

### INORGANIC PEROXY COMPOUNDS

#### CLASSIFICATION OF PEROXY COMPOUNDS

A large number of inorganic derivatives of hydrogen peroxide are known, including the peroxides of metals and non-metals, peroxy acids and peroxy salts, all of which contain oxygen in a so-called active or easily available form. The peroxides and peroxy acids may be visualized as derived from a parent compound,  $H_2O_2$ , by replacement of one or both of the hydrogen atoms by metal atoms or by acid radicals. Thus, replacement of the first hydrogen by a sodium atom yields  $Na-O-O-H$  (sodium hydroperoxide, a substance which is thermally rather unstable); and replacement of both hydrogens yields  $Na-O-O-Na$ , or the common peroxide of sodium. Likewise, the substitution of one or both hydrogens by the sulfonic acid radical,  $-SO_3H$ , yields peroxymonosulfuric acid,  $HSO_3-O-OH$ , and peroxydisulfuric acid,  $HSO_3-O-O-SO_3H$ .

It is to be recalled that true peroxides must contain the  $-O-O-$  linkage to establish their relationship to hydrogen peroxide, and that various oxides have been called peroxides which are not in a strict sense peroxides at all, lacking the bridged oxygen structure. Thus, silver forms the common oxide,  $Ag_2O$ , and also a black compound,  $AgO$ , which many older reference books list as "silver peroxide," frequently doubling the formula, as  $Ag_2O_2$ , in order to imply a closer relationship to hydrogen peroxide. However, this compound has been shown to contain divalent silver and is not directly derived from hydrogen peroxide, nor does it yield hydrogen peroxide when treated with an acid. Lead dioxide and manganese dioxide also may be found incorrectly referred to as peroxides. With dilute hydrochloric acid these compounds yield chlorine, rather than hydrogen per-

oxide, which would be expected to be formed from a true peroxide.\* The lead and manganese atoms are both tetravalent in these compounds, not divalent, as would be the case if they possessed the peroxide structure.

Therefore, to be properly classed as a metal peroxide, the substance concerned must be related to hydrogen peroxide not only in its composition, as, for example, a salt is related to its parent acid, but also in its structure, with the -O-O- grouping present. In the case of metal peroxides the  $O_2^-$  ion is present, which has an electronic configuration such as  $[\ddot{\text{O}}:\ddot{\text{O}}:]^-$ ; in contrast,  $\text{AgO}$ ,  $\text{PbO}_2$ , or  $\text{MnO}_2$ , all have the simple, doubly-charged  $[\text{O}]^=$  ion,  $[\text{O}]^=$ , in their structures.

In addition to these ions there is also the superoxide ion,  $O_2^-$ , which is found in a few compounds of strongly electro-positive metals, such as  $\text{NaO}_2$ ,  $\text{K}_2\text{O}_2$  and  $\text{BaO}_2$ . The electronic configuration of this ion is believed to be represented best by  $[\ddot{\text{O}}-\ddot{\text{O}}]^-$  (1). The parent acid related to these compounds,  $\text{HO}_2$ , has not been isolated.

Although, strictly speaking, superoxides belong to a separate class of compounds, it is useful to consider them in a discussion of peroxides, because of the similarity existing between the modes of formation and the reactions of the two types of compounds. Further details concerning the distinctive characteristics of the superoxides will be given below.

Electron diffraction measurements (2) carried out on the vapors of hydrogen peroxide lead to the conclusion that in the  $\text{H}_2\text{O}_2$  molecule the interatomic distance of the -O-O- grouping is  $1.47 \pm 0.02 \text{ \AA}$ , (see also Chapter 5). Corresponding data for crystalline hydrogen peroxide (3) lead to a closely similar value. The change in the character of the -O-O- grouping on going from hydrogen peroxide to other peroxy compounds is chiefly in its

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\* This test for the presence of the -O-O- grouping must be used with some caution; as, for example, the reaction of concentrated hydrochloric acid with barium peroxide yields some chlorine.

degree of electronegativity, or the degree to which it may be spoken of as ionic; the -O-O- bond itself appears to remain essentially unchanged. In metal peroxides, such as  $\text{BaO}_2$  or  $\text{SrO}_2$ , or in other peroxy compounds, the -O-O- distance found is apparently not appreciably different from that in hydrogen peroxide (although some earlier measurements (4, 5) led to lower values). Measurements on such peroxides as barium peroxide (6), ammonium and cesium peroxydisulfate (?), dimethyl peroxide (8), and dibenzoyl peroxide (9) buttress this conclusion.

In the superoxide ion, with one three-electron bond, the -O-O- distance becomes 1.29 Å (10); and in the oxygen molecule, with two three-electron bonds, the -O-O- distance is 1.21 Å (11). In ozone, the bond distance, 1.28 Å, is much the same as that in the superoxides ion (12). These changes are due to the differences in the -O-O- bonding.

Substitution of the hydrogens of hydrogen peroxide by metal atoms or acid radicals may well lead to a considerable change in the OOR angle and the azimuthal angle between the -OR groups. In the essentially ionic metal peroxides these angles, of course, are not concerned.

As indicated above, inasmuch as hydrogen peroxide has two replaceable hydrogens, it may function as a dibasic acid, and therefore may give rise to an intermediate type of compound, a hydroperoxide, such as  $\text{Na}-\text{O}-\text{O}-\text{H}$ , in which only one of the hydrogens has been replaced by a metal, as in an "acid salt."

In addition, some evidence exists indicating that the heavier and bulkier alkali metals, especially rubidium and cesium, may form peroxides of the type  $\text{M}_2\text{O}_3$ , which would lie between the  $\text{M}_2\text{O}_2$  and  $\text{MO}_2$  types of compounds (13). They may, indeed, actually represent combinations of superoxides and peroxides.

Formation of a peroxide by an element, with a consequent increase in the proportion of oxygen above that shown by the normal oxides of the element, does not imply an increase in the oxidation state of the element above that allowed by its

group position in the periodic classification. Thus, in the peroxide,  $TiO_3 \cdot 2H_2O$ , the oxidation number of the titanium is still +4, as it is in  $TiO_2$ . Again, in the case of a chromium peroxide,  $CrO_5$ , it has been considered that in addition to two peroxy groups,  $O_2^-$ , there is also present an ordinary  $O^=$  atom, so that the oxidation number of chromium remains at  $Cr^{+6}$ , just as it is in  $CrO_3$ . The authenticity of this peroxy compound however, is not free from doubt.

Tables 1 and 2 list the known peroxides and superoxides of the elements according to the group position of the elements in the Periodic Table.

TABLE I  
INORGANIC PEROXIDES  
(INCLUDING SUPEROXIDES)

Group I		Group II	
a	b	a	b
$H_2O_2$ ; $(HO_2)^*$			
$Li_2O_2$			
$Na_2O_2$ ; $NaO_2$		$(MgO_2 \cdot xH_2O)$	
$K_2O_2$ ; $(K_2O_3)$ ; $KO_2$ ; $(KO_3)^*$	$(CuO_2 \cdot H_2O)$	$CaO_2$ ; $(CaO_4)$	$(ZnO_2)$
$Rb_2O_2$ ; $(Rb_2O_3)$ ; $RbO_2$			
$Cs_2O_2$ ; $(Cs_2O_3)$ ; $CsO_2$		$SrO_2$ ; $(SrO_4)$	$(CdO_2)$
$(NH_4)_2O_2$		$BaO_2$ ; $(BaO_4)$	$(Hg_2O_2)$ ; $(HgO_2)$

\* Compounds in parentheses have not as yet been isolated in a pure state. The Table does not include the hydroperoxides, such as  $NaOOH$ , which, as above indicated, represents a type of compound intermediate between  $H_2O_2$  and  $Na_2O_2$ . The compound  $KO_3$ , reported by Whaley and Kleinberg (14) as resulting from the reaction of ozone with KOH, may possibly contain the ion  $O_3^-$  and thus represent a state of oxidation above the superoxide.

The outstanding importance of the compounds of the alkali and alkaline earth metals has suggested their presentation separately in Table 1. The incomplete character of much of our knowledge concerning the peroxides of other elements is clearly indicated in Table 2. In this latter Table the existence of peroxy acids of various elements or their salts, in Groups III to VI, of which as yet no peroxides have been isolated, is indicated by an asterisk, as in C\*.

In connection with the unsatisfactory nature of the status of numerous peroxides, as is clearly evident from a glance at the tables, it is of interest to note that Haissinsky (15) concluded that, with few exceptions, elements, the electronegativities of which were not greater than 2.1 (the value assigned to hydrogen), are capable of forming peroxidized compounds. Exceptions included such elements as carbon, nitrogen, sulfur and mercury. If valid, the application of such a rule would enable one to distinguish between genuine and spurious peroxy compounds.

In the case of a number of hydrated peroxyacids and their salts doubt has existed as to the mode of linkage of the peroxide grouping in these compounds; whether a pure peroxy-acid, with characteristic -O-O-H linkages, is present, together with hydrate water molecules, or whether the structure is that of a normal oxyacid with "hydrogen peroxide of hydroperoxidation" or, in the solid state, "hydrogen peroxide of crystallization." Thus sodium carbonate forms addition compounds with hydrogen peroxide, referred to more fully below, one of which approximates in composition the formula,  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$  (13, 16, 17). This substance is a white powder, which is quite stable under ordinary conditions. When protected from atmospheric moisture it suffers a loss of active oxygen content at room temperature. Such compounds are not strictly speaking salts of true peroxyacids, such as are represented by the formulas of hydrated peroxyzirconic or peroxytitanic acids,  $\text{H}_2\text{ZrO}_4 \cdot \text{H}_2\text{O}$  or  $\text{H}_2\text{TiO}_4 \cdot \text{H}_2\text{O}$ .\* It is apparent

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\* The supposed peroxyacids of silicon, germanium and thorium are likewise in this category.

TABLE 2  
INORGANIC PEROXIDES

III		IV		V	
a	b	a	b	a	b
B*		C*		(NO <sub>3</sub> ) (N <sub>2</sub> O <sub>7</sub> )	
(Y <sub>2</sub> O <sub>9</sub> ·nH <sub>2</sub> O)		Si*		P*	
(La <sub>4</sub> O <sub>9</sub> ·nH <sub>2</sub> O) <sup>t</sup>		TiO <sub>3</sub> ·2H <sub>2</sub> O		V*	
(La <sub>2</sub> O <sub>5</sub> ·nH <sub>2</sub> O) <sup>t</sup> or		ZrO <sub>3</sub> ·2H <sub>2</sub> O		Cr <sup>b*</sup>	
ThO <sub>3</sub> ·2H <sub>2</sub> O		HfO <sub>3</sub> ·2H <sub>2</sub> O	(SnO <sub>3</sub> ·nH <sub>2</sub> O)	Ta*	
		ThO <sub>3</sub> ·2H <sub>2</sub> O			
VI		VII		VIII	
a	b	a	b		
O <sub>3</sub> (O <sub>4</sub> <sup>2-</sup> )					
(SO <sub>4</sub> )		(ClO <sub>4</sub> ) <sub>2</sub>			
(CrO <sub>5</sub> )				(FeO <sub>2</sub> );(Fe <sub>2</sub> O <sub>6</sub> )	
Se*				(CoO <sub>2</sub> ·xH <sub>2</sub> O)	
Mo*				(NiO <sub>2</sub> ·xH <sub>2</sub> O)	
W*		(Re <sub>2</sub> O <sub>8</sub> )	((IO <sub>4</sub> ) <sub>2</sub> )		
UO <sub>4</sub> ·2H <sub>2</sub> O <sup>Δ</sup>					

\* Elements form peroxyacide, but peroxides not isolated.

<sup>t</sup> Of the rare earths, Ce gives CeO<sub>3</sub>·2H<sub>2</sub>O; Nd, Pr, Sm give hydrous compounds similar to those of La.

<sup>Δ</sup> Also NpO<sub>4</sub>·4H<sub>2</sub>O, PuO<sub>4</sub>·xH<sub>2</sub>O.

that the situation is complicated further by the fact that many compounds containing associated "hydrogen peroxide of crystallization" may also be hydrated. In the case of  $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ , formed from the hydroxide and alcoholic hydrogen peroxide, we find a true metal peroxide crystallizing with three molecules of hydrate water as well as hydrogen peroxide of crystallization. Similarly, the so-called "sodium perborate" of commerce is commonly represented as  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  (18). Further details concerning its preparation and applications are given below. Such addition compounds of hydrogen peroxide containing also hydrate water may be called hydrated hydroperoxides.

Stable, true peroxy compounds, such as potassium peroxydisulfate,  $\text{K}_2\text{S}_2\text{O}_8$ , when added to a potassium iodide solution at pH 7.5 to 8.0, will liberate iodine, but no oxygen is evolved. On the other hand, the addition type of compound, containing hydrogen peroxide of crystallization, and unstable peroxy compounds containing groupings which are easily hydrolyzed to form hydrogen peroxide and the normal oxyacid:  $-\text{O}-\text{OH} + \text{H}_2\text{O} \rightarrow -\text{OH} + \text{H}_2\text{O}_2$ , will not liberate iodine under these conditions, but instead the hydrogen peroxide released decomposes with evolution of oxygen. These facts have been utilized in a proposed test (19) for a true peroxy compound, as distinguished from the addition type of compound. The validity of this test, sometimes referred to as the Riesenfeld-Liebhafsky test, has been called into question recently by Partington (20). It would appear probable that the result of this test may be relied upon when iodine is liberated; but that if the test is negative--if oxygen, but no iodine, is set free--we are left in doubt whether an easily hydrolyzable peroxy compound or hydrogen peroxide of crystallization is responsible for the observed result.

Other examples of compounds containing hydrogen peroxide of crystallization, either in the anhydrous or hydrated state, include such compounds as:  $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2 \cdot 9\text{H}_2\text{O}$ ;  $\text{KF} \cdot \text{H}_2\text{O}_2$  (21);  $(\text{NH}_4)_2\text{SO}_4 \cdot \text{H}_2\text{O}_2$  (22);  $\text{Na}_2\text{SiO}_3 \cdot 2\text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  (23); and numerous others. The authenticity of some of these compounds must be considered

as not above question, resting in general upon the results of analysis of solids crystallized from mixtures of hydrogen peroxide with solutions of the respective salts. These substances in general are white, free-flowing solids, which have a moderate degree of solubility in water, the solutions giving the reactions of hydrogen peroxide. The fact that true peroxy salts may exist, as well as the respective hydrogen peroxide addition compounds, is indicated by the report that true peroxyborates may be isolated, which are very stable at room temperature (24).\*

#### PREPARATION OF INORGANIC PEROXIDES AND SUPEROXIDES

##### General Methods Leading to Peroxide Formation

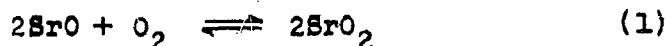
The procedure best suited to the preparation of a particular metal peroxide or superoxide is in general selected from one of three methods: (1) heating the metal or its oxide in oxygen or air; (2) oxidation in liquid ammonia; (3) reactions of compounds of the metal with hydrogen peroxide, usually in the presence of added alkali. In the first of these methods the metal may be heated in an excess of oxygen or air to the requisite temperature. By this method sodium is converted in two stages and 95% yield to the pale-yellow peroxide,  $\text{Na}_2\text{O}_2$ , when the metal is heated at about  $300^\circ\text{C}$  in dry air. The hydroperoxide,  $\text{NaOOH}$ , or its hydroperoxalate,  $\text{NaOOH} \cdot 0.5 \text{ H}_2\text{O}_2$ , is formed from an ice-cold alcoholic solution of  $\text{Na}_2\text{O}_2$  by addition of concentrated mineral acids. Of the other alkali metals under similar circumstances lithium gives the normal oxide,  $\text{Li}_2\text{O}$ , a white solid, with only traces of the peroxide, whereas potassium, rubidium and cesium yield superoxides-- $\text{KO}_2$ , orange-yellow;  $\text{RbO}_2$  and  $\text{CsO}_2$ , variously described as reddish yellow and dark brown.

In Group II, no peroxide of beryllium has been definitely

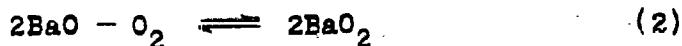
\* An addition product of hydrogen peroxide and a borate, together with sodium silicate is marketed under the name "sodium perbor silicate" (25). It has excellent storage characteristics when in contact with catalytically inactive materials. It is found valuable as a combined detergent, bleaching and cleansing agent.

established; and of the alkaline-earth family of metals only strontium and barium yield peroxides when the metal is heated in oxygen at atmospheric pressure, as  $\text{CaO}_2$  and  $\text{MgO}_2$  are thermodynamically unstable under these conditions. Strontium combines incompletely with oxygen to form a peroxide at  $500^\circ\text{C}$  under pressures of the order of 100 to 150 atm (26).\*

Under pressures of 200 - 250 atm and temperatures of  $350 - 400^\circ$  the reversibility of the reaction



has been demonstrated (27). The reversibility of the reaction of barium oxide with oxygen:



carried out at  $500 - 550^\circ\text{C}$ , was formerly applied to the separation of oxygen from the nitrogen of the air (Brin process), the control of the direction of the reaction being maintained by adjustment of the pressure of the gas in contact with the solid at this temperature.

A second general method by which peroxides of the alkali and alkaline-earth metals have been prepared differs from the first method in that the oxidation of these metals is effected in liquid ammonia solution (about  $-33^\circ\text{C}$  or lower). Thus, a solution of metallic sodium in liquid ammonia is converted by oxygen into the peroxide,  $\text{Na}_2\text{O}_2$ ; and of the other alkali metals, potassium, rubidium and cesium similarly form peroxides as the first step leading to the superoxides. However, lithium and, among

\* The dissociation pressure of  $\text{SrO}_2$  reaches 760 mm at  $357^\circ$ . It is of interest to note that, although solid strontium oxide does not take on additional oxygen at  $400^\circ$  and 100 atm pressure to more than about 15% of the amount theoretically required for complete conversion to peroxide, if a solution of strontia in fused caustic alkali is employed and oxygen passed into it, the peroxide may be formed practically completely. Leaching of the cooled melt with alcohol dissolves the caustic alkali, leaving slightly soluble strontium peroxide.

the alkaline-earth metals, calcium and magnesium, as well as beryllium, either fail to react in this manner or undergo incomplete conversion. The small size of the lithium and beryllium atoms doubtless contributes to their inability to form the corresponding metal peroxides under these conditions.

When a current of dry ammonia gas is passed into a cold solution of 98% hydrogen peroxide in absolute ether,\* a crystalline hydroperoxide,  $\text{NH}_4\text{OOH}$ , first separates at  $-10^\circ\text{C}$ , then redissolves as more ammonia is provided and ammonium peroxide,  $(\text{NH}_4)_2\text{O}_2$ , a colorless oil, freezing at about  $-40^\circ\text{C}$ , is formed.

Peroxides of some metals which are not formed under ordinary conditions by the direct action of oxygen on the metal (e.g., lithium peroxide) may be prepared in a third method by the addition of 30% hydrogen peroxide to concentrated aqueous solutions containing the metal ion. Solid  $\text{Li}_2\text{O}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$  is obtained when 30% hydrogen peroxide is added to a concentrated solution of lithium hydroxide, followed by the addition of alcohol. The anhydrous peroxide,  $\text{Li}_2\text{O}_2$ , can be obtained from the hydroperoxide by drying over phosphorus pentoxide in vacuo. Beryllium peroxide, however, is not obtainable by this procedure and magnesium yields a product containing a mixture of some peroxide with considerable hydroxide. The other alkaline-earth metals give hydrated compounds, such as  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{SrO}_2 \cdot 8\text{H}_2\text{O}$ , or  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ , of unknown crystal structures, which on dehydration yield the anhydrous compounds.

Some confusion exists in the literature concerning the existence of the intermediate type of oxide,  $\text{M}_2^{+1}\text{O}_3$  or  $\text{M}^{+2}\text{O}_3$ , such as  $\text{K}_2\text{O}_3$ ,  $\text{Rb}_2\text{O}_3$ , or  $\text{BaO}_3$ , presumed to be formed either when the superoxide is heated or by the action of oxygen on liquid ammonia solutions of the respective metals. In the latter case the oxidation of the metal, such as potassium, is considered to

\* As the mixture of 98% hydrogen peroxide in ether may be explosive under some circumstances, this procedure is attended with some danger.

pass through the stages represented by the formulae:  $K_2O_2$ ,  $K_2O_3$  and  $KO_2$ . Joannis (28) oxidized a solution of metallic potassium in liquid ammonia by passing a stream of oxygen through the solution until the precipitate formed assumed a definite, brick-red color, and before the change to yellow ( $KO_2$ ) had occurred. De Forcrand (29) heated the superoxide,  $KO_2$ , at  $480^\circ$  under 1 mm pressure and claimed that a product corresponding to pure  $K_2O_3$  was obtained thereby. Jaubert (30) claimed to have prepared the same substance by a controlled, slow oxidation of an alloy of potassium with lead, tin, or sodium, gently warmed as air was gradually admitted. The claim to chemical individuality of these intermediate oxides is not too well founded, however, and it is very probable that they may represent merely mixtures of the superoxides and peroxides; although some authors prefer to look upon them as possessing definite stoichiometrical compositions, indicated by such a formula as  $Rb_2O_2 \cdot 2RbO_2$ . X-ray studies on the rubidium and cesium compounds led to the formulation  $Rb_4O_6$  and  $Cs_4O_6$  for these substances (31). In the absence of any evidence of the existence of an  $O_3^-$  ion in such substances, the "sesquioxides" formulae must be regarded as of doubtful significance.

#### Preparation of Superoxides

As indicated above, the reaction of metallic potassium, rubidium, or cesium, heated with oxygen at ordinary pressure, or fused with potassium nitrate, leads in a vigorous manner directly to the superoxides, such as  $KO_2$ ; whereas the oxidation of sodium normally stops at the peroxide stage,  $Na_2O_2$ . The superoxides of potassium, rubidium and cesium are also obtained in a quite pure condition by the rapid oxidation of solutions of the metals in liquid ammonia.

Although early writers refer to potassium superoxide as if it were dimeric, as in  $K_2O_4$  (28), this formulation is not borne out by the x-ray study of the solid compounds. It has been shown conclusively that in the potassium compound the crystal is composed of an array of  $K^+$  and  $O_2^-$  ions in a face-centered

lattice of the calcium carbide type. The crystal structure of  $KO_2$ , like that of  $CaC_2$ , may be regarded as derived from the rock-salt type of structure by replacement of the  $Cl^-$  ion by the  $O_2^-$ , or  $C_2^=$  ion, respectively. In order to accommodate this replacement of  $O_2^-$  for  $Cl^-$  a lowering of the symmetry of the crystal to the tetragonal system becomes necessary. The compound is paramagnetic; the magnetic moment of 2 Bohr magnetons corresponds to a structure with one unpaired electron, as is indicated in its electronic formula. This evidence likewise serves to refute the dimeric formulation,  $K_2O_4$ .

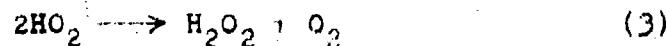
In the reaction products of 30% hydrogen peroxide acting upon the hydrated peroxides of barium and calcium, the presence of 8 to 9% of the superoxides of these metals has been reported, but the completely pure compounds,  $CaO_4$  or  $BaO_4$ , probably have not yet been isolated. Recent work by Schechter and Kleinberg *et al.* (32) has indicated that sodium also is capable of forming with oxygen a superoxide,  $NaO_2$ , at a temperature of approximately  $-77^\circ C$  in liquid ammonia solution. The compound reverts to the peroxide and oxygen when the temperature is allowed to rise. As yet no superoxide of lithium has been isolated, although evidence has been offered of its formation at temperatures well below the boiling point of liquid ammonia,  $-33^\circ C$  (33).

The superoxides are distinguished from the corresponding peroxides by the readiness with which they liberate oxygen when added to ice-cold water; under similar conditions the peroxides in general do not react in this way without the presence of a catalyst. Heating a dry superoxide, such as  $KO_2$ , does not cause appreciable loss of oxygen up to the melting point--in this case approximately  $400^\circ C$ . This degree of stability, of course, is not shared by  $NaO_2$ , which is presumably stable only at low temperatures.

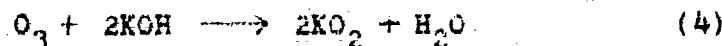
The vigorous reaction of potassium superoxide with water, liberating oxygen, has been utilized in the construction of gas masks employed in fire-fighting or rescue work, in which

the moisture and carbon dioxide in the exhaled breath of the wearer of the mask, reacting with the superoxide contained in the canister of the gas mask, releases a supply of oxygen sufficient for the wearer's need and converts the carbon dioxide into potassium carbonate. In this way the mask may operate as in a closed system, entirely independent of the surrounding atmosphere.

Just as all metal peroxides are considered as salts of the parent acid,  $H_2O_2$ , so the superoxides may be referred to as salts of an unstable acid,  $HO_2$ , which when released, spontaneously decomposes into hydrogen peroxide and oxygen:



It is also probable that the reaction of ozone upon solid potassium hydroxide, which results in a yellowish-brown solid coating, is due to the formation of potassium superoxide:



A rather surprisingly violent reaction between potassium superoxide and metallic potassium has been described by Gilbert (34). A crust of the oxides of potassium,  $1/4" - 1/2"$  thick, formed by the gradual action of atmospheric oxygen upon stored bars of the metal, when brought forcibly into intimate contact with the underlying metal (presumably beneath a layer of the monoxide, which normally acts as an insulator) resulted in a violent explosion, which was interpreted as being due to interaction of the metal and the superoxide contained in the outer layer. This behavior is not duplicated by sodium, which on slow oxidation by gradual access of air forms no superoxide, but mainly the monoxide.

In a commercial preparation of potassium superoxide the molten metal is sprayed into a chamber containing a mixture of oxygen and nitrogen (13 to 35%  $O_2$ ) under conditions such that the product is rapidly solidified as a light powder. Further details concerning the properties of this compound are given below.

A wide variation in thermal stability is shown by the metal peroxides, ranging from the relatively very stable compounds of the alkali metals, through the alkaline earth peroxides and zinc and cadmium peroxides to the relatively unstable compounds of copper and mercury, this order following the decrease in electropositive character of the constituent metals. Details concerning the individual compounds are given below.

Considering the properties and applications of individual metal peroxides, in the following account these compounds are listed in the order of their location in the Periodic Table.

#### PEROXY COMPOUNDS OF GROUP I

Of the alkali metals the peroxide of sodium and the superoxide of potassium are the only compounds of practical importance.

##### Sodium Peroxide

$\text{Na}_2\text{O}_2$ , the commonest and best known of the metal peroxides, usually prepared by the action of dry, carbon dioxide-free air, or oxygen, upon metallic sodium, best at  $300 - 400^\circ\text{C}$ , is commercially available as a yellowish-white powder with a content of 90 - 95%  $\text{Na}_2\text{O}_2$ . The oxidation may be conducted either in a continuous manner, in which sodium metal is heated as it is brought into an atmosphere progressively richer in oxygen, or in a two-step process, wherein the monoxide is first formed under conditions of limited access of oxygen and low temperature ( $120 - 200^\circ\text{C}$ ), followed subsequently by the conversion of the monoxide to peroxide in a furnace at  $200 - 390^\circ\text{C}$ , in which the powdered monoxide is kept in constant motion in an atmosphere of either pure oxygen or dry air enriched with oxygen. Utilization of rotary furnaces in place of conventional stationary kilns in this process has been found to effect a considerable saving of space and of labor. Nantz (35) has recommended a process involving exposure of sodium oxide to cyclically varying pressure of dry air at  $350 - 490^\circ$ .

The yellowish color of sodium peroxide has been considered by some writers to be due to impurities, such as iron. However, on heating, the color of pure sodium peroxide deepens to a brown, and on cooling the original color is restored. This behavior resembles that of the oxides of zinc, tin, indium, etc. When superficially converted to carbonate, by contact with air, as may occur when the solid has been allowed to stand some time in a container which is not tightly sealed, the yellow color is accordingly converted to white. Above its melting point ( $460^{\circ}\text{C}$ ) decomposition with loss of oxygen becomes noticeable and at red heat progresses readily (36).

Atmospheric moisture and carbon dioxide are rapidly absorbed by sodium peroxide, with formation of hydroxide and carbonate, respectively. The reaction of solid sodium peroxide with liquid water at ordinary temperature is a vigorous one, resulting in the liberation of oxygen and a strong heating effect; but if ice-cold water is used and the solid is added gradually, these effects may be largely avoided, and the resulting alkaline solution at room temperature shows the presence of hydrogen peroxide. At higher temperatures the hydrogen peroxide rapidly decomposes in the presence of the free alkali.

In its various applications sodium peroxide thus acts as a convenient source of hydrogen peroxide when brought into solution. If sodium peroxide is brought at room temperature into contact with carbon dioxide-free air, saturated with water vapor, or dissolved in about four times its weight of ice-cold water, an octahydrate,  $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$ , may be obtained, which deposits as clear, transparent, tabular crystals when the solution is evaporated. At  $30^{\circ}$  the hydrate dissolves in its crystal water; but at temperatures above  $40^{\circ}\text{C}$  the alkaline solution begins to decompose. A mono- and a dihydrate are also known. Vapor pressures of water over sodium peroxide hydrates have been reported by Busse (37).

The formation of sodium hydroxide and hydrogen peroxide by the hydrolysis of sodium peroxide is the basis of one

of the largest uses of this compound, for bleaching and laundry purposes. Wood pulps, cotton, linen and wool, straw, oils, glue and gelatine, and various other materials may be bleached by the use of sodium peroxide. Commercial preparations for such purposes usually contain stabilizers, such as sodium silicate or magnesium sulfate. The decomposition of hydrogen peroxide, thus formed, from sodium peroxide, which is favored by the presence of alkali, is also utilized as a convenient source of small quantities of oxygen.

Sodium peroxide has a variety of uses as an oxidizing agent, both in industry and in the analytical laboratory. In the latter, fused sodium peroxide, either alone or when mixed with the proper proportion of sugar charcoal, provides a most powerful oxidizing fusion reagent, which attacks many refractory materials (38). Fusions of this kind are usually carried out in nickel or silver crucibles--platinum being rapidly attacked under most ordinary conditions.\* Iron is somewhat more resistant, but aluminum or copper are rapidly attacked by the fused peroxide.

Although of itself sodium peroxide is seen to be a relatively quite stable substance below its melting point and is not subject to explosive decomposition through shock or heating in a flame, nevertheless, mixtures of the peroxide with a wide variety of easily oxidizable materials, both organic and inorganic, lead to some explosive reactions. A mixture of sodium peroxide with iron filings, aluminum powder, calcium carbide, or sulfur powder, when moistened with water or concentrated sulfuric acid, or when heated strongly, may result in an explosion; and under similar circumstances violent explosions or reactions with incandescence are shown by a number of organic substances, such as sugar, glycerine, glacial acetic acid, and ether. Wood, paper, or cloth may be caused to ignite by contact with sodium peroxide.

\* Rafter (39) has pointed out that, in the absence of easily oxidizable materials, such as sulfides, and if the preliminary heating is carried out cautiously so that the temperature does not exceed 270°C before the reaction proper sets underway, the maximum temperature attained will, in general not exceed 540°C, and under these circumstances the platinum will not be attacked.

Oxidations of various lower valence compounds, such as chromic and manganous salts, to chromate and manganese dioxide respectively, occur readily; and iron powder is converted directly to sodium ferrate,  $\text{Na}_2\text{FeO}_4$ . Nitric or nitrous oxides react at about  $150^\circ\text{C}$  with sodium peroxide to form sodium nitrite and, in the latter case, free nitrogen.

Organic peroxides and peroxyacids have been prepared by the interaction of sodium peroxide with organic acid anhydrides or acid chlorides under suitable conditions.

Sodium peroxide not only forms hydrates, but, as mentioned above, when treated in the cold with an alcoholic solution of concentrated sulfuric, hydrochloric, or nitric acid, it forms the "acid salt,"  $\text{NaOOH}$ , sodium hydroperoxide, which is a rather unstable, crystalline, white solid. The hydroperoxide itself is capable of forming a hydroperoxidate, as in  $2\text{NaOOH}\cdot\text{H}_2\text{O}_2$  and its hydrated form,  $2\text{NaOOH}\cdot\text{H}_2\text{O}_2\cdot4\text{H}_2\text{O}$ . These compounds are too unstable to find use commercially. Analogous compounds of potassium are also known.

#### Potassium Peroxide and Superoxide

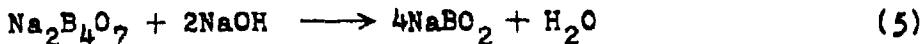
Like sodium, potassium is capable of forming a peroxide,  $\text{K}_2\text{O}_2$ , a sulfur-yellow, hygroscopic powder, resulting, e.g., from the oxidation of potassium metal, dissolved in liquid ammonia, by passage of oxygen through the solution at  $-50^\circ\text{C}$ , until the solution becomes decolorized. When the peroxide is heated in air or oxygen it is converted into the superoxide,  $\text{KO}_2$ . The product of the oxidation of metallic potassium when warmed in oxygen or air to  $60 - 80^\circ\text{C}$  is consequently, the superoxide,  $\text{KO}_2$ , chrome-yellow in color. The superoxide is also produced by the low-temperature oxidation of potassium in liquid ammonia with an excess of oxygen. Potassium superoxide is quite stable on heating up to its melting point,  $380^\circ\text{C}$ . At higher temperatures it dissociates, forming  $\text{K}_2\text{O}_2$  and oxygen. Atmospheric moisture rapidly decomposes it with formation of potassium hydroxide and with liberation of oxygen; with liquid water it reacts intensely in the same manner. It reacts both with carbon dioxide and with carbon monoxide to form carbonate and oxygen.

Rubidium and cesium form similar superoxides. All are deep yellow in color, darkening to brown on heating, and turning black when melted.

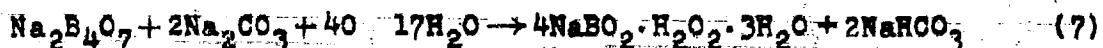
### Peroxy Salts of Group I Metals

Among the peroxy salts of Group I metals, the peroxyborates, peroxycarbonates and peroxyphosphates, referred to earlier, may be considered as typical.

Sodium peroxyborate may be prepared (40) by the reaction of borax solution with hydrogen peroxide and sodium hydroxide (or sodium peroxide), as in



or by the electrolysis (41) of a solution of borax and sodium carbonate, using platinum anodes:



The hydrated compound which precipitates on cooling the solution to about  $10^{\circ}\text{C}$  may be filtered off, washed and dried. Preparation as a barium salt has <sup>also</sup> been described (42). It serves as a source of hydrogen peroxide in an alkaline medium (pH of saturated solution is about 10), and has found extensive use not only in textile bleaching and the oxidation of dyestuffs, but in tooth powders, oral antiseptics, etc. Its properties are those corresponding to an addition product of hydrogen peroxide rather than to a salt of some hypothetical peroxyboric acid. It is therefore preferably represented by the formulation used above, that of the trihydrated hydroperoxide of sodium metaborate, rather than as the tetrahydrate of a peroxyborate,  $\text{NaBO}_3$ .

Similarly, when a solution of hydrogen peroxide and sodium carbonate containing the proper proportions of the two compounds, is evaporated, or when hydrogen peroxide is added to a concentrated solution of sodium carbonate, the hydroperoxide,  $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ , is precipitated (43). This substance holds its hydrogen peroxide content rather constantly at room temperature over considerable periods of time. The white solid contains

about 14% of active oxygen and is frequently used in cleasing agents, with soaps, detergents, etc., especially for home laundering.

Several other addition compounds of sodium carbonate and hydrogen peroxide, together with their hydrates, have been reported, including compounds with ratios of  $H_2O_2:H_2O$  of 1:1 and 2:1. The thermal and dehydration characteristics of these hydrated hydroperoxides have been studied by Makarov and Chamova (44).

These substances are, of course, not salts of true peroxycarbonic acid. Of the latter, the potassium compound,  $K_2C_2O_6$ , potassium peroxycarbonate, was first prepared in 1896 (45) by the electrolysis (46) of a saturated solution of potassium carbonate at  $-15^{\circ}C$ . The structure of this compound, and similarly that of sodium and rubidium, contains the  $[C_2O_6]^{2-}$  ion, which may be represented as  $\begin{array}{c} [ -O-C-O-O-C-O- ]^{2-} \\ \quad \quad \quad \quad \quad \end{array}$ . The salt, which in a moist condition is pale blue in color, is reasonably stable when preserved in a dry atmosphere, but is easily decomposed by the moisture of ordinary air, yielding  $CO_2$  and oxygen, and reverting to potassium carbonate.

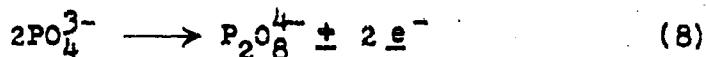
The true peroxycarbonates of sodium, potassium and rubidium were also prepared by the action of fluorine gas on the corresponding carbonate solutions at  $-13^{\circ}$  to  $-16^{\circ}C$ , with regular addition of alkali hydroxide solutions (47). The stability of the resulting peroxycarbonates is dependent in large measure upon the purity of the starting materials. Absence of even minute quantities of catalytic ions, such as affect the stability of hydrogen peroxide itself, is essential.

The formation of peroxycarbonic acids in salt solutions containing oxygen and carbon dioxide has been observed polarographically (48). Partington and Fathallah (24) reviewed and reinvestigated the subject of peroxycarbonates.

From sodium pyrophosphate the compound,  $Na_4P_2O_7 \cdot 2H_2O_2$ , is obtained by the action (49) of concentrated hydrogen peroxide

on a slurry of the pyrophosphate. Its properties resemble those of the preceding addition compounds. Numerous hydrogen peroxide addition compounds of alkali, ammonium, and alkaline-earth orthophosphates, especially the secondary and tertiary salts, have been prepared by direct interaction of the constituent compounds.

In a manner analogous to that exhibited by the sulfates and carbonates, it has been possible to prepare true peroxyphosphates, particularly by the electrolytic method. Thus, potassium peroxyphosphate,  $K_4P_2O_8$ , is formed at the anode when a solution of phosphate,  $K_2HPO_4$  is electrolyzed (50), the essential reaction being

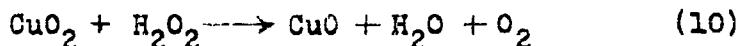
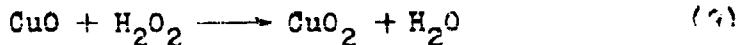


The peroxyphosphates also result from the reaction of fluorine upon aqueous solutions of disodium phosphate or pyrophosphate (51). The solid salt is quite stable, but its solutions undergo hydrolysis, more rapidly than those of the persulfates, forming hydrogen peroxide and phosphoric acid.

Peroxyacids, or their salts, formed from various other elements in Groups IV to VI of the periodic system have been reported, for details concerning which the reader is referred to Machu's book.

In periodic Group Ib, although reference has been made to the fact that the so-called peroxide of silver is believed not to be a true peroxide, but merely an oxide of divalent silver,  $Ag_2O$ , it is barely possible that a peroxide of univalent silver is capable of existence. Existing data leave the matter still in doubt.

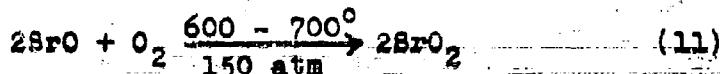
A hydrated, red peroxide of copper is known,  $CuO_2 \cdot H_2O$ , as well as a basic compound reported to be  $CuO_2 \cdot Cu(OH)_2$  (52). The existence of such substances as these offers a reasonable explanation of the pronounced catalytic effect of cupric compounds upon the decomposition of hydrogen peroxide, in which a cycle of changes represented by such equations as



may be responsible for the sharp increase in the rate of decomposition of the peroxide caused by the presence of copper compounds. This subject has been investigated by Glasner (53).

#### PEROXY COMPOUNDS OF GROUP II

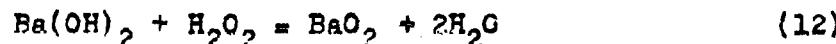
The alkaline-earth metals, calcium, strontium and barium (but probably not beryllium) form peroxides, which may be made, in the case of barium and strontium, by either wet or dry methods. In the dry way, for example, the reaction



produces strontium peroxide in 90 - 95% purity. Barium peroxide does not require additional pressure for conversion from the monoxide to be effected. The dry process yields a denser product than precipitation in the wet way, as by addition of hydrogen peroxide to a solution of the nitrate, referred to below. Magnesium peroxide apparently cannot be prepared directly from the oxide. The formation of  $\text{CaO}_2$  from calcium oxide and oxygen was first reported by Struve (54) and data are available for the dissociation pressures at low temperatures (55). Riesenfeld and Nottebohm (56) failed to achieve synthesis in this manner, however, and the situation is complicated by the fact that the peroxide appears to have two modifications, an alpha form, stable at low temperatures and slow to dissociate, and a beta form stable at higher temperatures and readily dissociable (55). Recent studies on the  $\text{CaO} - \text{O}_2$  system have shown that traces of the peroxide are formed at low temperatures and high pressures (57).

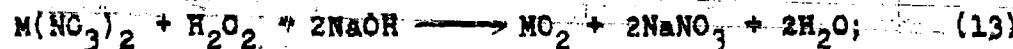
These peroxides are capable of adding up to eight molecules of water, to give hydrated peroxides, such as  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ . The hydrated peroxides result from the interaction of a slurry

of the metal hydroxide or salt (58) with concentrated solutions of hydrogen peroxide, in a reaction which is essentially the reverse of the process whereby hydrogen peroxide is produced by the hydrolysis of a metal peroxide:

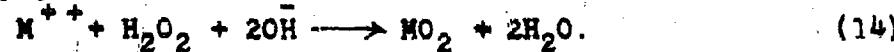


In any event, the water of hydration is rather loosely held, and may be driven off by cautious heating without causing decomposition of the peroxide. As a group the peroxides lose oxygen fairly easily above  $200^\circ$  to  $250^\circ\text{C}$ , but barium peroxide is stable in air up to about  $700^\circ\text{C}$  (see below).

In place of the slurry of metal hydroxide, a solution of the nitrate of the metal may be caused to react with hydrogen peroxide in the presence of alkali:



or, more simply:



If the solution is cooled, the octahydrate,  $\text{MO}_2 \cdot 8\text{H}_2\text{O}$ , may crystallize out as the solid phase, whereas at higher temperatures the anhydrous peroxide may result. The hydrated crystals are more easily filtered and washed than the slimy anhydrous peroxide precipitates, but they lose active oxygen more readily on dehydration than the anhydrous compounds.

The monohydroperoxidated compounds, such as  $\text{BaO}_2 \cdot \text{H}_2\text{O}_2$ , formed when cold concentrated hydrogen peroxide acts upon the dioxide, lose their hydrogen peroxide of crystallization on warming. The magnesium compound, although capable of existence, has not been isolated in a pure condition.

Although the alkaline-earth peroxides are sufficiently stable and unreactive when dry to be stored for years at ordinary temperatures without appreciable deterioration, nevertheless, when in contact with combustible matter, especially if ground

with such matter, they may cause fires.

Additional data concerning the individual compounds in Group II, follow.

#### Barium Peroxide

Barium peroxide in Group IIa is the most important and most stable of the peroxides of the alkaline earths, and is probably the oldest known peroxide, having been studied long before hydrogen peroxide was first observed. Prior to the development of the electrolytic process for preparing hydrogen peroxide, it served as the chief source of this compound. Recently a renewal of industrial interest in this early process has been noted, and several large-scale plants have been built or are projected in this country for the production of non-electrolytic hydrogen peroxide. The preparation of barium peroxide by the reversible process



was the basis of the now-obsolete Brin process for the manufacture of oxygen which was employed prior to the present-day process utilizing the fractional distillation of liquid air. Roasting the monoxide in air at  $600 - 700^\circ$  readily forms the peroxide,  $\text{BaO}_2$ . The process is reversible; increasing pressure favors the formation of the peroxide, while increasing temperature displaces the equilibrium toward the left. The dissociation pressure reaches 760 mm at  $840^\circ$  (59). Traces of moisture (resulting in formation of barium hydroxide) are found necessary to catalyze both the decomposition of the peroxide and its formation from the monoxide and oxygen. The temperature of dissociation at atmospheric pressure is lowered by the catalytic effect of added oxides, according to Kendall and Fuchs (60).

When pure, barium peroxide is a white powder of sp. gr. 4.96; as supplied commercially, it may have a slight yellowish tinge if traces of iron have not been eliminated. The commercially available barium and strontium peroxides contain varying quanti-

ties of the oxides or hydroxides. When heated at atmospheric pressure, but in the absence of moisture, barium peroxide should be stable up to about  $740^{\circ}\text{C}$ , at which temperature its dissociation pressure equals  $1/5$  atm. Due to its progressively increasing decomposition pressures at still higher temperatures, its melting point has not been established, but the mass, now a mixture of dioxide and monoxide, softens at about  $800^{\circ}\text{C}$ , and is freely fluid at bright red heat.

As previously indicated, barium peroxide forms the well-defined octahydrate,  $\text{BaO}_2 \cdot 8\text{H}_2\text{O}$ ; for example, when dilute hydrogen peroxide is mixed with a saturated solution of barium hydroxide. It forms glistening flaky crystals which readily effloresce and are slightly soluble in water (about 1 g per liter at room temperature), with some decomposition into the original reactants.

Besides its formerly important uses as a starting material for the preparation of dilute hydrogen peroxide solutions and of oxygen, and consequently its employment in bleaching and disinfecting, barium peroxide, because of its good oxidizing action, has found use in pyrotechnics (green flame), and when mixed with magnesium powder, in ignition mixtures, such as those used to initiate the thermite reaction.

#### Calcium and Magnesium Peroxides

The peroxides of calcium and magnesium (in general admixed with hydroxide) have found utilization in bleaching and disinfecting (for example, in the storing of grain or seed, and in the dressing of wounds); calcium peroxide has also been used in dentifrices, cosmetics, and even in chewing gum. In baking, considerable quantities of  $\text{CaO}_2$  are used as an aid in the mechanical handling of dough. Both magnesium and calcium peroxides have been employed as internal antacids and anti-fermentatives. They are white powders, generally available not as pure compounds but containing 40 to 50% of oxide. They are quite stable and may be kept for years at ordinary temperatures when dry; but are decomposed rapidly above  $300^{\circ}\text{C}$ , a few hours' heating at  $350^{\circ}$  suf-

ficing to bring about a total loss of their active oxygen content. The hydrate,  $\text{CaO}_2 \cdot 8\text{H}_2\text{O}$ , is precipitated when hydrogen peroxide is added to a solution of calcium hydroxide (or when sodium peroxide is added to a solution of a calcium salt). It becomes anhydrous when heated to  $130^\circ$  and is completely decomposed into oxide and oxygen below red heat.

#### Zinc Peroxide

$\text{ZnO}_2$ , like magnesium and calcium peroxides, has been generally available only in the form of a mixture containing about 45 - 50% of the hydroxide. It may be made by the reaction of a thin slurry of zinc oxide with hydrogen peroxide (61). A more nearly pure product is obtained by the reaction of zinc ethyl or zinc amide with hydrogen peroxide in ether solution. When pure it is a white powder, but the commercial product may be slightly yellow in color. The compound decomposes when warmed and deflagrates above  $200^\circ\text{C}$ . It is only slightly hydrolyzed by water, and is valuable as an antiseptic and astringent, when used alone or in conjunction with sulfa drugs in the treatment of wounds and skin diseases. It is a frequent ingredient in cosmetics, deodorants, salves and dusting powders. It has also found application in the preparation of insecticides and in the vulcanizing of rubber.

#### Cadmium Peroxide

$\text{CdO}_2$ , a yellow powder, usually obtained in an impure form as a basic compound,  $x\text{CdO}_2 \cdot y\text{Cd}(\text{OH})_2$ , by methods similar to those used for the preparation of zinc peroxide, like the latter is completely decomposed above  $180^\circ\text{C}$ . This compound is not utilized commercially at the present time.

#### Mercury Peroxide

Mercury is reported as forming a very unstable, brick-red mercuric peroxide,  $\text{HgO}_2$ , resembling red phosphorus, prepared either by the action of 30% hydrogen peroxide on an alcoholic mercuric chloride solution, followed by addition of alkali, or by the action of 30% hydrogen peroxide on red mercuric oxide.

This peroxide is one of the most easily decomposable of the inorganic peroxides which are isolable in the solid condition. It explodes when rapidly heated or on shock. At ordinary temperatures or even at 0°C it quickly decomposes into red mercuric oxide and oxygen. In water it vigorously sets free oxygen and forms yellow mercuric oxide while some hydrogen peroxide is produced in the solution. Less well established is the reported formation of a mercurous peroxide,  $Hg_2O_2$ , by addition of concentrated hydrogen peroxide to mercurous oxide at low temperature.

#### PEROXY COMPOUNDS OF GROUPS III - VIII

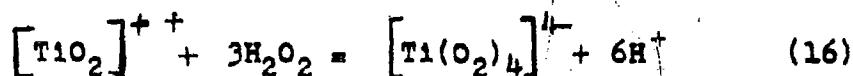
##### Yttrium and the Rare Earths

In Group III, hydrous peroxides are reported for yttrium, lanthanum, cerium, and some of the other rare earth metals. Yttrium peroxide is said to have the composition  $Y_4O_9 \cdot nH_2O$ . Cerium forms red-brown  $CeO_3 \cdot 2H_2O$ , a suggested structure of which has been represented as  $(HO)_3CeO - OH$ . Titanium, zirconium, hafnium, and thorium in Group IVa form similar compounds, that of titanium possessing a characteristic yellow color, the others being white. The compositions of the peroxides of the other rare earth elements have not been established beyond question. There is found for lanthanum, neodymium, praseodymium, and samarium some uncertainty between the general formula,  $R_4O_9 \cdot nH_2O$  and  $R_2O_5 \cdot nH_2O$ . By heating in oxygen under high pressure, praseodymium oxide is said to be converted into the dioxide,  $PrO_2$ , although under ordinary conditions the product approximates the composition  $Pr_6O_{11}$ .

##### Titanium, Zirconium, Hafnium and Thorium

The most well-defined peroxide type of metals in Group IVa is the hydrated trioxide,  $MO_3 \cdot 2H_2O$ , (62), which, as stated, is common to all members of this sub-group. The intense yellow to orange-red color resulting from the addition of hydrogen peroxide to titanium solutions in the pres-

ence of dilute sulfuric acid is a familiar useful qualitative test for hydrogen peroxide. Schwarz and Giese (63) believe these peroxides correspond to a formulation similar to the ceric compound,  $M^{4+}(OH)_3(OOH)$ . The titanium derivative, soluble in potassium hydroxide in the presence of hydrogen peroxide, forms such products as  $K_4TiO_8 \cdot 6H_2O$ , a salt of the ortho-acid  $H_4Ti(O_2)_4$ . In acid solution, the intense yellow color produced by addition of hydrogen peroxide to a titanium solution is considered (64) to be due to the peroxidized titanyl ion  $[TiO_2 \cdot xH_2O]^{++}$ , which is related to the peroxy anion present alkaline solution through the equilibrium:



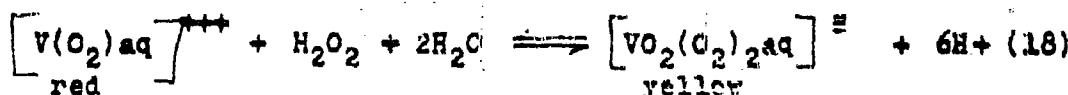
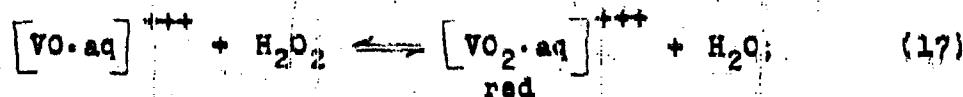
It has been possible also to prepare a series of peroxytitanates of still higher oxygen content, such as  $Na_2TiO_5 \cdot 3H_2O$  (65) and  $(NH_4)_2TiO_5 \cdot H_2O$  (18). The sodium compound has also been represented as  $TiO_2 \cdot Na_2O_2 \cdot 2H_2O$ , although such formulas give little information concerning the actual molecular structure of the compound concerned. Similarly, zirconium yields peroxyzirconates, such as  $K_4ZrO_8 \cdot 6H_2O$  and  $Na_4Zr_2O_{11} \cdot 9H_2O$ ; but the corresponding hafnium salts and the thorium salts are not known. The hydrated peroxides,  $HfO_3 \cdot 2H_2O$  (66) and  $ThO_3 \cdot 2H_2O$  (67), however, have been prepared from hafnium and thorium solutions, respectively.

#### Vanadium, Niobium and Tantalum

In conformity with the rule that the stability of peroxyacids of elements in any periodic sub-group increases with increasing atomic weight of the elements in the group, it is noted that in Group Va the stability of the peroxyacids increases from vanadium to tantalum. The anhydrous peroxides themselves, however, do not appear to have been isolated in a pure state. Arsenic, antimony and bismuth, in the b sub-group, appear not to form peroxides.

Elements in Group Va show a generally similar behavior toward hydrogen peroxide resembling that of titanium and zirconium.

A number of peroxyvanadates have been prepared by the interaction of hydrogen peroxide with vanadate solutions in acid or alkaline medium. The resulting compounds have colors ranging from yellow to red, a fact which may serve as the basis of a sensitive test for hydrogen peroxide. Peroxyvanadic acid itself has not been isolated; and most of the peroxy-compounds of vanadium are easily decomposed. When hydrogen peroxide is added to a solution of a vanadyl salt, such as  $[VO]_2[SO_4]_3$  (which is formed when vanadium pentoxide is dissolved in moderately concentrated sulfuric acid), a dark red-brown color is produced, due to a peroxyvanadyl compound, such as  $[V-O-O]_2[SO_4]_3$ . Jahr (64) concluded that when pentavalent vanadium reacts with hydrogen peroxide, two peroxy compounds result, which in solution enter into the following equilibria:



Crystalline peroxyvanadates of reasonably definite composition have been reported by reactions of  $V_2O_5$  of an orthovanadate with alkaline solutions of hydrogen peroxide, including  $Na_3VO_8$  and  $KH_2VO_6 \cdot H_2O$ . The rate of hydrolysis of vanadium peroxide was found (68) to be slow relative to that for molybdenum or tungsten peroxides.

The peroxyniobates are somewhat more stable than the peroxyvanadates; and the free acid,  $H_4NbO_5 \cdot \text{aq}$ , monoperoxyniobic acid, has been isolated as a pale yellow solid. Alkaline solutions of alkali or alkaline-earth niobates react with hydrogen peroxide to form a series of peroxyniobates, such as  $K_3NbO_8$ , or  $K_4Nb_2O_{11} \cdot 3H_2O$ , some of which are hydrated, others anhydrous.

The peroxytantalates, such as  $\text{Na}_3\text{TaO}_8 \cdot 14\text{H}_2\text{O}$  and  $\text{K}_3\text{TaO}_8$ , resemble the corresponding niobium compounds, and the solid hydrous-free acid,  $\text{H}[\text{TaO}_4]\text{aq}$ , is obtainable from a solution of potassium peroxytantalate by treatment with sulfuric acid. It withstands heating to  $100^\circ$  without appreciable decomposition.

#### Chromium, Molybdenum, Tungsten and Uranium

In Group VIa, chromium forms a number of peroxy-compounds, including the blue peroxide,  $\text{CrO}_5$ , which is soluble in ether and forms addition compounds with organic bases (such as pyridine). Two series of peroxy salts of chromium are clearly distinguishable, the blue salts of the type,  $M\text{CrO}_6$ , such as  $\text{KCrO}_6 \cdot \text{H}_2\text{O}$ , formed when another solution of  $\text{CrO}_5$  is added to alkaline alcoholic  $\text{H}_2\text{O}_2$ , and the red salts of the type  $M_3\text{CrO}_8$  formed by a chromate and an alkaline  $\text{H}_2\text{O}_2$ , which are isomorphous with the peroxyvanadates.

In the red salts, such as  $\text{K}_3\text{CrO}_8$ , Wilson (5) concluded that the structure of the  $\text{CrO}_8^{3-}$  anion is tetrahedral, with a chromium atom at the body center and four  $\text{O}_2$  groups, the centers of which are located at the apices of the tetrahedron. The peroxy-niobates and peroxytantalates also possess the same crystal structure, so that it is conceivable that the oxidation state of the chromium in the red salts is likewise five. The blue potassium salt is diamagnetic, and to avoid an odd number of electrons its molecule is considered to be dimeric, as in  $\text{M}_2[\text{OCr}(\text{O}_2)_2-\text{O}-\text{O}-\text{Cr}(\text{O}_2)_2-\text{O}]$  with hexavalent chromium. The peroxide,  $\text{CrO}_5$ , does not form salts when treated with alkalies; instead, the compound decomposes. Its structure is believed to contain two  $\text{O}_2$  groups, as in  $\text{O} \leftarrow \text{Cr} \begin{array}{l} \nearrow \text{O}_2 \\ \searrow \end{array}$ , with hexavalent chromium (63). The peroxide grouping  $\text{CrO}_2$  is represented by Sidgwick (69) as  $\text{Cr} \rightarrow \text{O} \rightarrow \text{O}$ , or  $\text{Cr} = \text{O} \rightarrow \text{O}$ , in preference to the closed ring,  $\text{Cr} \begin{array}{l} \nearrow \text{O} \\ \searrow \end{array}$ . Beltrán Martinez and Porter (70) have proposed the formula  $\text{Ca}_3\text{Cr}_2\text{O}_{15} \cdot 10\text{H}_2\text{O}$  for the red peroxychromate of calcium.

An additional type of peroxy-compound, brown in color, contains the grouping  $\text{CrO}_4$ , as in  $\text{CrO}_4 \cdot 3\text{NH}_3$ , formed by addition

of hydrogen peroxide to ammoniacal chromate solutions, at 0° and subsequent warming to 50°. Its structure is represented as  $(\text{NH}_3)_3\text{Cr} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix} \begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \end{smallmatrix}$ . Addition of potassium cyanide to its aqueous solution yields  $\text{CrO}_4 \cdot 3\text{KCN}$ . It is not known definitely whether chromium is hexavalent or tetravalent in these compounds. Glasner (71) has discussed the formation and constitution of the peroxychromates.

Unlike chromium, molybdenum forms a peroxyacid,  $\text{H}_2\text{MoO}_5 \cdot 1.5\text{H}_2\text{O}$ , when  $\text{MoO}_3$  and  $\text{H}_2\text{O}_2$  interact; the product is a yellow solid, insoluble in ether. As with chromium, however, several sets of peroxy salts appear to exist, such as the yellow peroxytungstates ( $\text{M}_2\text{MoO}_6$ ) and the unstable red salts ( $\text{M}_2\text{MoO}_8$ ). The situation is rendered complex by virtue of the fact that polymolybdates are formed in strongly acid molybdate solutions and these in turn may become peroxidized (72).

Tungsten peroxyacids and their salts are more stable than those of chromium or molybdenum, and suffer decomposition only very gradually at ordinary temperatures (73). Colorless compounds, containing the  $\text{HWO}_6^-$  ion, and yellow substances, yielding the  $\text{WO}_8^{2-}$  ion, are known. Judging from the intensity of the yellow color produced, Rumpf-Nordmann (74) concluded that maximum peroxy salt formation occurs when the molar ratio of hydrogen peroxide to sodium tungstate is 2.0. Polyperoxytungstates are also known, analogous to the polyperoxymolybdates. Their structures have not been reported. Jahr and Blanke (75) suggested the existence of the ion  $[\text{W}_2\text{O}_3(\text{C}_2\text{H}_5)_4 \text{aq}]^{\pm}$ .

Uranium forms the yellow, hydrated peroxide,  $\text{UO}_4 \cdot 2\text{H}_2\text{O}$ , stable below 100°; sometimes incorrectly referred to as "peruranic acid." This compound has been shown to be non-ionized and therefore may not properly be regarded as the parent acid of the peroxyuranate salts. The uranium peroxide is easily formed by the simultaneous addition of hydrogen peroxide and base to a pH controlled solution of uranyl sulfate (76). Compounds with univalent metals of the types  $\text{M}_4\text{UO}_4$ ,  $\text{M}_2\text{UO}_6$  and  $\text{M}_6\text{U}_2\text{O}_{18}$  have been

reported. The transuranic elements, neptunium and plutonium (67) are similarly credited with hydrous peroxides,  $\text{NpO}_4 \cdot x\text{H}_2\text{O}$  and  $\text{PuO}_4 \cdot x\text{H}_2\text{O}$ . Connick and MoVey (77) reported the existence of two peroxy complexes of Pu (IV), one brown, the other red. Possible structures were suggested and it was determined that these compounds contained more than 1 plutonium ion per molecule.

#### Other Metals

Of the remaining metals, reports of various peroxides are not lacking, but are for the most part not too convincing. Thus, a compound,  $\text{Re}_2\text{O}_8$ , that is,  $\text{O}_3\text{Re}-\text{O}-\text{O}-\text{ReO}_3$ , or a peroxidized  $\text{Re}_2\text{O}_7$ , was described by the Noddacks (25) as white and unstable in the presence of water; but cannot be considered as definitely established. Again, although iron has not yielded a pure peroxide, the existence of such a compound as an intermediate, formed in oxidation reactions involving hydrogen peroxide in the presence of ferric ion, is not unlikely. A red substance, supposed to be  $\text{FeO}_2$ , is reported as formed by the action of hydrogen peroxide at low temperature upon hydrous ferric oxide suspended in alcohol; and more highly oxygenated compounds, such as  $\text{FeO}_3$  and even  $\text{FeO}_4$ , have been claimed by different investigators.

A hydrous dioxide of cobalt,  $\text{CoO}_2 \cdot x\text{H}_2\text{O}$ , has been said to result from the action of excess sodium hypochlorite upon dilute cobaltous sulfate solution in the presence of sodium sulfate. The analogous green nickel compound,  $\text{NiO}_2 \cdot x\text{H}_2\text{O}$ , is said to be formed from precipitated nickelous hydroxide by means of hydrogen peroxide; but may be merely an addition compound of nickelous hydroxide and hydrogen peroxide. Its properties differ from those of anhydrous, black  $\text{NiO}_2$ , in which nickel is tetravalent.

#### Peroxides of Non-Metals

Among the non-metals a few unstable and little-known peroxides are to be found, including  $\text{NO}_3$  (and possibly  $\text{N}_2\text{O}_7$ ), for which only spectroscopic evidence is available;  $\text{SO}_4$ , prepared, for example, by the action of fluorine upon sulfuric

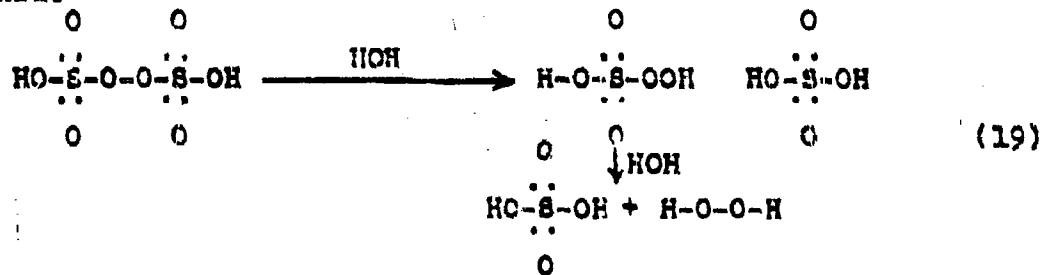
acid or alkali, sulfate at low temperatures; and the peroxides of chlorine and iodine, such as  $\text{ClO}_4$  (or  $\text{Cl}_2\text{O}_8$ ), resulting from the reaction of silver perchlorate and iodine in ether or benzene solution, but known only in dilute solution. Up to the present time these substances have appeared to have little practical importance.

### PEROXY ACIDS AND THEIR SALTS

#### Peroxydisulfuric Acid

Peroxydisulfuric acid,  $\text{H}_2\text{S}_2\text{O}_8$  (sometimes called persulfuric acid or Marshall's acid), is a white, crystalline solid, melting with decomposition at about  $65^\circ$ . It is manufactured as an intermediate in the manufacture of hydrogen peroxide by one of the electrolytic methods. In this process it is used in solution, and is not isolated. As described in Chapter 3, a solution of sulfuric acid (approximately 10 N) is electrolyzed with platinum anodes at high current densities, passing in succession through a series of cells and emerging as a solution approximately 2.5 N in peroxydisulfuric acid.

Hydrolysis of the warm acid solution yields hydrogen peroxide



with intermediate formation of peroxymonosulfuric (Caro's) acid,  $\text{H}_2\text{SO}_5$ .

The structure of the  $\text{S}_2\text{O}_8^{2-}$  ion has been established (79) by x-ray analysis of the cesium and the ammonium salts, as two  $\text{SO}_4$  tetrahedra joined at the points in an O-O linkage.

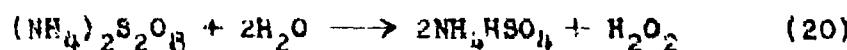
Although solutions of peroxydisulfuric acid are reason-

ably stable when kept cool, they are rapidly hydrolyzed when boiled in the presence of excess sulfuric acid. Because of this hydrolytic tendency, as well as the actively oxidizing character of the compound, peroxydisulfuric acid is difficult to obtain in a very pure condition, and is not usually isolated from its solutions. Various organic materials are attacked by the acid; paraffin is charred, and mixture with some organic solvents may even lead to explosion.

When freshly prepared, solutions of the acid at room temperature do not exhibit the characteristic reactions of hydrogen peroxide with titanium solution or permanganate, and iodine is liberated only slowly from an iodide solution. The powerfully oxidizing character of peroxydisulfate is demonstrated, however, by the conversion of manganous ion into permanganate (aided catalytically by a trace of silver ion). The chief practical interest in peroxydisulfuric acid is in its role in the manufacture of hydrogen peroxide by the electrolytic process, as above indicated. Some application has been made of peroxydisulfates in certain organic oxidations.

#### Salts of Peroxydisulfuric Acid

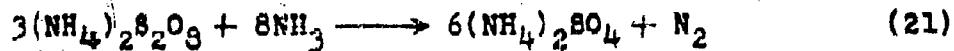
Among the salts of peroxydisulfuric acid, the ammonium and potassium salts,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  and  $\text{K}_2\text{S}_2\text{O}_8$ , are of chief importance. They are crystalline, white solids. The potassium salt is especially stable in ordinary air; the ammonium compound also keeps well in a dry atmosphere, but is liable to cake in moist air, as it is somewhat hygroscopic. Ammonium peroxydisulfate is much more soluble than the potassium salt--the respective solubilities at 0° being 58 and 1.8 gm per 100 g  $\text{H}_2\text{O}$ --so that the potassium salt may be precipitated by addition of potassium bisulfate solution to a solution of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ . Aqueous solutions of both salts slowly hydrolyze at room temperature yielding hydrogen peroxide and other products. Thus,



Other peroxydisulfate salts are formed by electrolytic oxidation of sulfates (80). A solution of ammonium peroxydisulfate is obtained at the anode when an ammonium bisulfate solution is electrolyzed with platinum anodes, and the peroxydisulfate is crystallized directly from the solution, washed and dried. The handling and shipping of this substance and of potassium peroxydisulfate are not considered to be attended by fire or explosion hazards, and wooden or fiberboard containers are frequently employed (17).

Barium peroxydisulfate,  $\text{BaS}_2\text{O}_8$ , in sharp contrast with the sulfate, is soluble in water. Among the uses of these compounds the bleaching of fats and of soap, the oxidation of some dyestuffs and the promotion of certain polymerization processes, especially in the synthetic rubber industry, may be mentioned.\*

In the presence of catalytic traces of silver salts, ammonium peroxydisulfate effects various oxidation processes, such as the oxidation of ammonia to nitrogen:



Thiosulfates are oxidized to tri- or tetrathionates, and metals like copper are dissolved, forming sulfates.

Potassium peroxydisulfate (commonly called potassium persulfate),  $\text{K}_2\text{S}_2\text{O}_8$ , is in many respects similar to the corresponding ammonium salt. It is, however, much less soluble (a saturated solution at  $0^\circ\text{C}$  contains about 2%, and at  $20^\circ\text{C}$  about 5%, of solid  $\text{K}_2\text{S}_2\text{O}_8$ ); and it is likewise more stable in contact with the air than the ammonium compound. The commercial preparation of the salt consists of adding a solution of potassium bisulfate to the solution of ammonium peroxydisulfate resulting

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\* A useful bibliography of the various uses of peroxy sulfates has been prepared by the Buffalo Electro-Chemical Co., Inc. (81). See also the monograph by Price (82).

from the electrolysis of ammonium bisulfate solution; the precipitated potassium peroxydisulfate is then centrifuged to separate it from the ammonium bisulfate mother liquid.

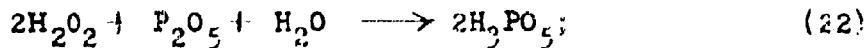
The largest use of potassium peroxydisulfate is as a polymerization promoter in the manufacture of artificial rubber. It has been applied to various other processes, such as the bleaching of fats and the oxidation of dyestuffs (17). A silver peroxydisulfate has also been reported (83).

#### Peroxymonosulfuric Acid

Peroxymonosulfuric acid, Caro's acid,  $H_2SO_5$  or  $HO-SO_2-O_2OH$ , was seen in the preceding section to be formed intermediate between peroxydisulfuric acid and the ultimate hydrolysis products, sulfuric acid and hydrogen peroxide. Like the parent peroxydisulfuric acid, this substance is hardly ever prepared in the pure state, due to its instability and reactivity toward oxidizable material. When obtained in the acid hydrolysis of peroxydisulfates, or by the reaction of concentrated hydrogen peroxide upon sulfuric acid, it is found to be a white solid, melting about  $45^{\circ}C$ . It is differentiated from hydrogen peroxide by means of the fact that its addition to an iodide solution causes an immediate liberation of iodine, whereas other types of peroxygen compounds react only rather slowly. Like peroxydisulfuric acid, but unlike hydrogen peroxide, Caro's acid does not react with potassium permanganate. Solutions of Caro's acid find their principal application in various organic oxidation processes.

#### Other Peroxy Acids

Other peroxyacids and their salts are known, which result from the action of hydrogen peroxide upon the appropriate anion or acid anhydride or by anodic oxidation processes. Thus peroxymonophosphoric acid,  $H_3PO_5$ , (analogous to Caro's acid) is formed when cold, concentrated  $H_2O_2$  is added to  $F_2O_5$  or  $HPO_3$  (84):

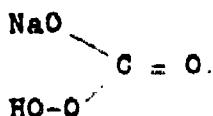


or by the anodic oxidation of solutions of orthophosphoric acid. Derivatives of the type  $\text{M}_4\text{P}_2\text{O}_8$  are also known analogous to the peroxydisulfates. The potassium salt is obtainable in the solid state.

Among other elements are to be found such compounds as the peroxy derivatives of the carbonates, germanates, and stannates.

In a manner quite analogous to that employed in the preparation of peroxydisulfates, electrolysis of concentrated potassium or rubidium carbonate solution at  $-10^\circ$  yields at the anode light-blue peroxycarbonates,  $\text{K}_2\text{C}_2\text{O}_6$  or  $\text{Rb}_2\text{C}_2\text{O}_6$ , which presumably have the structure:  $\text{MOOC-O-O-COOM}$ . The interaction of an alkali carbonate solution at low temperature with elementary fluorine likewise yields the peroxycompounds (47).

Other types of peroxycarbonates have been reported, such as  $\text{Na}_2\text{CO}_4$  (24), which is formed when phosgene reacts with  $\text{Na}_2\text{O}_2$ , with liberation of oxygen. Action of carbon dioxide on sodium peroxide, or on an alcoholic solution of  $\text{NaOOH}$ , is reported to yield another peroxydicarbonate,  $\text{Na}_2\text{C}_2\text{O}_6$ , isomeric with the product of an electrolytic method of preparation, as well as a possible peroxybicarbonate,  $\text{NaHCO}_4$ , which presumably would be represented as



The structures of these substances have not been definitely established; but seem reasonably to be as indicated.

Peroxyacids of other Group IV elements include those of titanium, germanium and tin. Peroxytitanic acid is written either as  $(\text{HO})_3\text{Ti}-\text{OOH}$ , or more commonly as the hydrated peroxyde,  $\text{TiO}_3 \cdot 2\text{H}_2\text{O}$ ; the deep yellow color of which results from the reaction of hydrogen peroxide on a solution of a titanium com-

pound, and is used familiarly as qualitative test for hydrogen peroxide.

Precipitated hydrous stannic oxide forms with concentrated hydrogen peroxide a product considered to be peroxydistannic acid,  $H_2Sn_2O_7$ ; analogously the compound  $K_2Ge_2O_7 \cdot 4H_2O$  peroxydigermanic acid, is said to result from the reaction of hydrogen peroxide with a solution of a metagermanate. Group Va elements including vanadium, niobium and tantalum are not credited with peroxides, but in solution form with hydrogen peroxide peroxy anions. The deep yellow of an acidified vanadate solution in the presence of hydrogen peroxide, which is employed, like the corresponding titanium reaction, for the detection of hydrogen peroxide, is due to such a cause. The peroxyniobate and peroxytantalate of potassium,  $K_3NbO_8$  and  $K_3TaO_8$ , resemble the red peroxychromate,  $K_2CrO_8$ , formed from a slightly alkaline chromate solution by addition of hydrogen peroxide in the cold.

One of the most widely used qualitative tests for hydrogen peroxide is based upon the formation of the deep blue peroxychromic acid when hydrogen peroxide is added to an acidified solution of a chromate. The acid is usually written as  $HCrO_5$ . Less well known are the corresponding peroxy compounds of the other Group VIA metals, molybdenum and tungsten. Peroxyanions of these elements have been reported by reactions similar to those employed in the case of the preceding elements.

A peroxynitric acid,  $HNO_4$ , formed when anhydrous  $H_2O_2$  reacts at low temperature with nitrogen pentoxyde, was reported by d'Ans (85) in 1911; but inasmuch as the substance is unstable even at low temperature, it has not been obtained in a pure condition; neither have stable salts been isolated. Other reported methods of synthesis of peroxy nitrates, such as the action of ozone on alkali azides (86) or of fluorine with dilute sodium nitrite solutions, are of questionable character (87).

It has not been attempted to make the discussion of inorganic peroxy compounds given in this chapter an exhaustive one.

For further details the reviews already cited (17, 82) as well as those by Neumark (88) and Slater (89) and the book by Machu (90) should be consulted.

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